needles leaving a completely colorless supernatant solution. The crystals were collected and found to be optically pure.

cis-(+)-$[\mathrm{Co(diars)_2CO_3}]^+$ → _cis_-(+)-$[\mathrm{Co(diars)_2Cl_2}]^+$. *cis*-(+)-$[\mathrm{Co(diars)_2CO_3}]\mathrm{ClO_4}$ (0.01 g) was dissolved in water (10 ml) and 2 drops of concentrated HCl was added. Carbon dioxide was quickly liberated and the solution turned brown and after 2 days at 25° deposited the *cis*-(+)-$[\mathrm{Co(diars)_2Cl_2}]\mathrm{ClO_4}$ salt quantitatively. It was collected and found to be optically pure.

cis-(+)-$[\mathrm{Co(diars)_2OH(OH_2)}]^{2+}$ → _cis_-(+)-$[\mathrm{Co(diars)_2(OH_2)_2}]^{3+}$. A 10^{-3} *M* solution of the *cis*-(+)-$[\mathrm{Co(diars)_2OH(OH_2)}](\mathrm{ClO_4})_2$ salt was made up in 1.0 *N* $\mathrm{HClO_4}$. The circular dichroism spectrum was the same as that of the pure diaquo complex.

cis-(−)-$[\mathrm{Co(diars)_2(NO_2)_2}]^+$ → _cis_-(+)-$[\mathrm{Co(diars)_2Cl_2}]^+$. *cis*-(−)-$[\mathrm{Co(diars)_2(NO_2)_2}]\mathrm{ClO_4}$ (0.009 g) was dissolved in HCl (10 ml; 5 M) containing a few crystals of urea. The solution slowly turned brown and after it stood at room temperature for 20 hr, 2 drops of concentrated $\mathrm{HClO_4}$ was added. After a further 2 days the crystals of the *cis*-dichloro complex were filtered from the colorless supernatant solution. The product was optically pure.

cis-(+)-$[\mathrm{Co(diars)_2(NO_3)_2}]^+$ → _cis_-(+)-$[\mathrm{Co(diars)_2Cl_2}]^+$. Exactly the same procedure was used for interconverting the dinitrato complex as that described for the dinitro complex except that urea was not added. The product was optically pure.

cis-(+)-$[\mathrm{Co(diars)_2(OH_2)_2}]^{3+}$ → _cis_-$[\mathrm{Co(diars)_2(OH)_2}]^+$. When the diaquo complex is dissolved in 0.1 *M* NaOH solution, a constant absorption and circular dichroism spectrum is obtained of the pink dihydroxo complex. Addition of $\mathrm{HClO_4}$ regenerates the diaquo species with full retention of activity.

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Registry No. *trans*-$[\mathrm{Co(diars)_2Cl_2}]\mathrm{Cl}$, 14170-33-3; *cis*-$[\mathrm{Co(diars)_2Cl_2}]\mathrm{Cl}$, 50804-93-8; *cis*-$[\mathrm{Co(diars)_2CO_3}]\mathrm{ClO_4}$, 51017-98-2; *cis*-$[\mathrm{Co(diars)_2(OH_2)_2}](\mathrm{ClO_4})_3$, 50804-95-0; *cis*-$[\mathrm{Co(diars)_2Cl_2}]\mathrm{ClO_4}$, 14170-34-4; $\mathrm{H_2C_2O_4}$, 144-62-7; *cis*-$[\mathrm{Co(diars)_2C_2O_4}]\mathrm{B(C_6H_5)_4}$, 51017-99-3; *cis*-$[\mathrm{Co(diars)_2(NO_3)_2}]\mathrm{ClO_4}$, 50804-97-2; *cis*-$[\mathrm{Co(diars)_2(NO_2)_2}]\mathrm{ClO_4}$, 51014-57-4; $\mathrm{CH_3CN}$, 75-05-8; *cis*-$[\mathrm{Co(diars)_2(CH_3CN)_2}](\mathrm{ClO_4})_3$, 50804-99-4; *cis*-(+)-$[\mathrm{Co(diars)_2Cl_2}]\mathrm{AsOC_4H_4O_6}$, 51050-98-7; *cis*-(+)-$[\mathrm{Co(diars)_2Cl_2}]\mathrm{Cl}$, 51050-99-8; *cis*-(−)-$[\mathrm{Co(diars)_2Cl_2}]\mathrm{Cl}$, 51051-00-4; *cis*-(+)-$[\mathrm{Co(diars)_2Cl_2}]\mathrm{ClO_4}$, 51051-01-5; *cis*-(−)-$[\mathrm{Co(diars)_2Cl_2}]\mathrm{ClO_4}$, 50805-01-1; *cis*-(+)-$[\mathrm{Co(diars)_2(OH_2)_2}](\mathrm{ClO_4})_3$, 51018-01-0; *cis*-(−)-$[\mathrm{Co(diars)_2(OH_2)_2}](\mathrm{ClO_4})_3$, 51020-04-3; *cis*-(+)-$[\mathrm{Co(diars)_2CO_3}]\mathrm{ClO_4}$, 51018-03-2; *cis*-(+)-$[\mathrm{Co(diars)_2(NO_3)_2}]\mathrm{ClO_4}$, 51063-05-9; *cis*-(−)-$[\mathrm{Co(diars)_2(NO_2)_2}]\mathrm{ClO_4}$, 50805-03-3; *cis*-$[\mathrm{Co(diars)_2(OH)(CH_3CN)}](\mathrm{ClO_4})_2$, 50805-05-5.

Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

Small Cobalt and Nickel Metallocarboranes from 2,3-$\mathrm{C_2B_4H_8}$ and 1,6-$\mathrm{C_2B_4H_6}$. Sandwich Complexes of the Cyclic $\mathrm{C_2B_3H_7}^{2-}$ and $\mathrm{C_2B_3H_5}^{4-}$ Ligands

RUSSELL N. GRIMES,* DON C. BEER, LARRY G. SNEDDON, VERNON R. MILLER, and RICHARD WEISS

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The reaction of $\mathrm{Na^+C_2B_4H_7^-}$ with $\mathrm{CoCl_2}$ and $\mathrm{NaC_5H_5}$ followed by exposure to air, water, and acetone gives (π-2,3-$\mathrm{C_2B_4H_6}$)Co(π-$\mathrm{C_5H_5}$), (π-2,3-$\mathrm{C_2B_3H_7}$)Co(π-$\mathrm{C_5H_5}$), and (π-2,3-$\mathrm{C_2B_3H_5}$)$\mathrm{Co_2}$(π-$\mathrm{C_5H_5}$)$_2$. *C*-Methyl and *C,C′*-dimethyl derivatives are obtained by analogous reactions of $\mathrm{Na^+CH_3C_2B_4H_6^-}$ and $\mathrm{Na^+(CH_3)_2C_2B_4H_5^-}$. Work-up of the parent metallocarborane products in 1 *M* HCl increases the yield of the four-boron species. Bridge deprotonation of (π-2,3-$\mathrm{C_2B_3H_7}$)Co(π-$\mathrm{C_5H_5}$) by NaH gives the $(\mathrm{C_2B_3H_6})\mathrm{Co(C_5H_5)}^-$ anion, which on reaction with $\mathrm{CoCl_2}$ and $\mathrm{NaC_5H_5}$ yields (π-2,3-$\mathrm{C_2B_3H_5}$)$\mathrm{Co_2}$(π-$\mathrm{C_5H_5}$)$_2$; treatment of the anion with HCl regenerates $(\mathrm{C_2B_3H_7})\mathrm{Co(C_5H_5)}$. Reduction of 1,6-$\mathrm{C_2B_4H_6}$ with sodium naphthalide followed by reaction with $\mathrm{CoCl_2}$, $\mathrm{NaC_5H_5}$, air, and water gives (π-2,4-$\mathrm{C_2B_3H_5}$)$\mathrm{Co_2}$(π-$\mathrm{C_5H_5}$)$_2$, (π-$\mathrm{C_2B_4H_6}$)$\mathrm{Co_2}$(π-$\mathrm{C_5H_5}$)$_2$, and [σ-5-(1-$\mathrm{C_{10}H_7}$)(π-2,4-$\mathrm{C_2B_4H_5}$)]Co(π-$\mathrm{C_5H_5}$), but only a trace of (π-2,4-$\mathrm{C_2B_4H_6}$)Co(π-$\mathrm{C_5H_5}$). The yield of the latter compound is improved by shorter reaction time. A similar reaction employing 2,3-$\mathrm{C_2B_4H_8}$ in place of 1,6-$\mathrm{C_2B_4H_6}$ gives the same products as in the reaction of $\mathrm{Na^+C_2B_4H_7^-}$ described above, except that only a trace of (π-2,3-$\mathrm{C_2B_4H_6}$)Co(π-$\mathrm{C_5H_5}$) is obtained. The reaction of 2,4-$\mathrm{C_2B_5H_7}$ with sodium naphthalide and $\mathrm{CoCl_2}$ gives a probable (π-2,4-$\mathrm{C_2B_4H_6}$)$_2\mathrm{Co}^-$ anion which was isolated as the tetramethylammonium salt. Reaction of $\mathrm{Na^+C_2B_4H_7^-}$ with bis(diphenylphosphino)ethanenickel(II) chloride gives (π-2,3-$\mathrm{C_2B_4H_6}$)$\mathrm{Ni[(C_6H_5)_2PCH_2]_2}$. Reaction of $\mathrm{Na^+C_2B_4H_7^-}$ with $\mathrm{NiBr_2}$, $\mathrm{NaC_5H_5}$, HCl, and air yields (π-$\mathrm{C_2B_5H_7}$)$\mathrm{Ni_2}$(π-$\mathrm{C_5H_5}$)$_2$ which is postulated to have an opened or distorted tricapped trigonal-prismatic structure.

Introduction

Previous work has shown that a variety of small cobalt[1,2] and iron[3-6] metallocarboranes can be synthesized from the lower carboranes *nido*-2,3-$\mathrm{C_2B_4H_8}$ and *closo*-$\mathrm{C_2B_5H_7}$, and a manganese[7] species has been obtained from *nido*-$\mathrm{CH_3C_3B_3H_6}$. Several of these syntheses[1,5] utilized methods previously applied to the large carboranes, particularly the opening of a polyhedral cage by electron transfer with subsequent metal insertion (polyhedral expansion) as developed extensively by Hawthorne and coworkers.[8-10] In other cases, metallocarboranes have been obtained from the small carboranes by new preparative routes such as the gas-phase incorporation of metals into closo[5,6] and nido[3,5,7,11,12] cages. Our interest in further exploration of the small metallocarboranes has been stimulated by the discovery of the cyclocarboranyl sandwich complexes,[2,3,5] which contain cyclic planar boron-carbon ligands analogous to the cyclopentadienyl system. The prototype compound, (π-$\mathrm{C_2B_3H_7}$)$\mathrm{Fe(CO)_3}$, was pre-

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pared in gas-phase reactions of $Fe(CO)_5$ with the nido carboranes $C_2B_4H_8$ [3,5] or $C_2B_3H_7$,[12] and the symmetrical Fe-ring sandwich bonding was confirmed in an X-ray study.[13] Subsequent work involving formation of cobalt and nickel metallocarboranes in solution has disclosed an extensive chemistry of the formal $C_2B_3H_7^{2-}$ ligand and its bridge-deprotonated derivatives, 2,3- and 2,4-$C_2B_3H_5^{4-}$, which form triple-decked bimetallic sandwich complexes as described in a recent communication.[2] These cyclocarboranyl complexes are formed, together with other metallocarboranes, from *nido*-$C_2B_4H_8$ or *closo*-1,6-$C_2B_4H_6$ *via* several different synthetic routes in which the product distribution is highly sensitive to reaction conditions. We report here the details of this chemistry and the structural characterization of the metallocarboranes obtained.

Results and Discussion

Cobalt Metallocarboranes from $Na^+C_2B_4H_7^-$. On combining separately prepared tetrahydrofuran (THF) solutions of $Na^+C_2B_4H_7^-$, sodium cyclopentadienide, and anhydrous cobalt(II) chloride in an air-free environment, stirring the mixture for several hours, evaporating to dryness, treating with water and acetone in air, and finally separating the products *via* column and thin-layer chromatography, the principal metallocarboranes obtained are (π-2,3-$C_2B_4H_6$)Co(π-C_5H_5) (I), a cyclocarboranyl sandwich (π-2,3-$C_2B_3H_7$)Co(π-C_5H_5) (II), and a triple-decked dicobalt complex (π-2,3-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$ (III), as depicted in Figure 1. Analogous reactions of the *C*-methylcarboranes $Na^+CH_3C_2B_4H_6^-$ and $Na^+(CH_3)_2C_2B_4H_5^-$ give the respective *C*-monomethylmetallocarborane derivatives, Ia, IIa, and IIIa, and the *C,C'*-dimethyl species Ib and IIIb. The *C,C'*-dimethyl derivative of II (IIb) has not been isolated.

The structures of I-III shown in Figure 1 have been assigned from ^{11}B and ^1H nmr spectra (Tables I and II), infrared spectra (Table III), and unit- and high-resolution mass spectra (Experimental Section) supported by X-ray studies of $CH_3GaC_2B_4H_6$ [11] and ($C_2B_3H_7$)Fe(CO)$_3$ [13] (analogs of I and II, respectively) and of (π-2-CH_3-2,3-$C_2B_3H_4$)Co_2(π-C_5H_5)$_2$ [2] (IIIa, shown in Figure 2). These structures are discussed in detail in a later section.

The relative yields of I-III are strongly dependent upon conditions extant during the reaction and in subsequent treatment, and it is clear that II is formed at least in part by degradation of I during the work-up of the complexes in aqueous media. The presence of high acid concentration during this treatment inhibits such degradation, considerably enhancing the yield of I; thus, following work-up in neutral water the yields of I-III were respectively 10, 16, and 3% of theory, while a separate experiment in which 1 *M* HCl was used gave 63, 4, and 2% of the respective compounds. In basic media such as KOH in ethanol, I is completely degraded to II, III, and traces of other products. The base hydrolysis of the small cobaltacarboranes has been examined in detail and will be reported elsewhere.[14]

Bridge Deprotonation of (π-$C_2B_3H_7$)Co(π-C_5H_5) and Conversion to (π-2,3-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$. The isoelectronic analogy between 2,3-$C_2B_4H_8$ and (π-$C_2B_3H_7$)Co(π-C_5H_5), II (which may be seen by formally replacing the apex BH unit in the former molecule with a (C_5H_5)Co group), suggested possible similarities in their chemistry. Accordingly, the bridge protons in II were expected to exhibit acidic behavior with respect to interaction with hydride ion. The re-

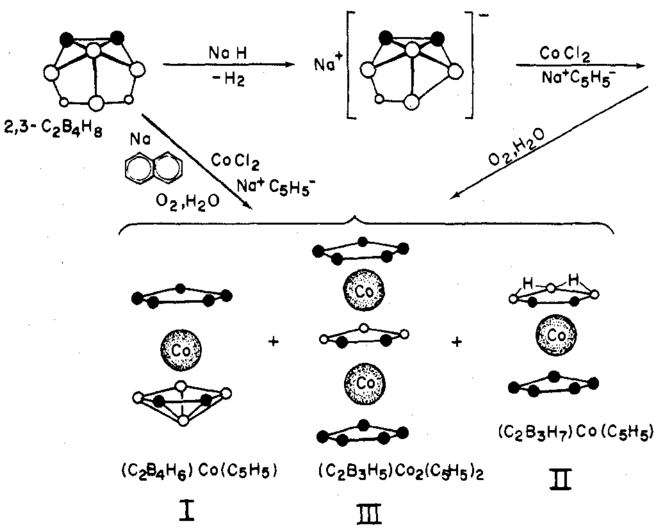

Figure 1. Reaction scheme for the synthesis of cobalt metallocarboranes I-III from 2,3-$C_2B_4H_8$, indicating the proposed structures of I and II and the assumed structure of III based on its *C*-methyl derivative, IIIa. Relative ring orientations depicted are arbitrary. Open circles are BH groups; solid circles, CH groups. Numbering in the pentagonal-pyramidal and pentagonal-bipyramidal cage systems is the same as in Figure 2.

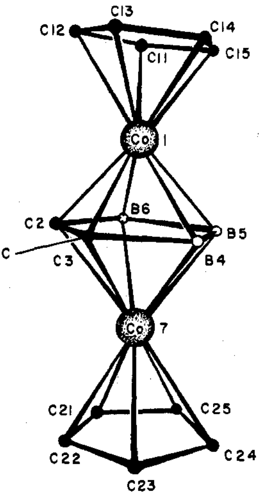

Figure 2. Established structure of the triple-decked complex (π-C-CH_3-$C_2B_3H_4$)Co_2(π-C_5H_5)$_2$, IIIa.

action with NaH was found to proceed readily in THF (Figure 3); as in the case of $C_2B_4H_8$,[15] only one bridge proton is removed, as shown by the production of just slightly more than 1 molar equiv of H_2 even during prolonged reaction (however, as is also true of $C_2B_4H_8$ or $C_2B_4H_7^-$, the remaining bridge hydrogen is removed in reactions which effect closure of the carborane cage,[3-5,11] such as that with $CoCl_2$ described below). The deprotonation is reversible, and addition of HCl or DCl to a solution of the [(π-$C_2B_3H_6$)Co(π-C_5H_5)]$^-$ anion regenerates II or its monodeuterio analog.

The reaction of Na^+[(π-$C_2B_3H_6$)Co(π-C_5H_5)]$^-$ with excess $CoCl_2$ and NaC_5H_5 in THF and subsequent treatment with water and air form the previously described[2] triple-decked complex (π-2,3-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$, III, in moderate yield (Figure 3).

Cobalt Metallocarboranes from *closo*-1,6-$C_2B_4H_6$ and *nido*-2,3-$C_2B_4H_8$ *via* Sodium Naphthalide Reduction. The reaction of a polyhedral carborane with sodium naphthalide in an

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Table I. 32.1-MHz ^{11}B Nmr Data

Compd	Solvent	δ,[a] ppm (J, Hz)	Rel areas
$(2,3\text{-}C_2B_4H_6)Co(C_5H_5)$, I	CCl_4	−13.1 (154), −6.8 (149), −2.3 (143)	1, 1, 2
$(2\text{-}CH_3\text{-}2,3\text{-}C_2B_4H_5)Co(C_5H_5)$, Ia	CCl_4	−13.1 (154), −8.0 (161), −3.0 (161)	1, 1, 2
$(2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_4H_4)Co(C_5H_5)$, Ib	CCl_4	−10.8 (173), −5.5 (170)	2, 2
$(2,3\text{-}C_2B_3H_7)Co(C_5H_5)$, II	CCl_4	−2.7 (149), −2.0 (147)	~2, ~1[b]
$(2\text{-}CH_3\text{-}2,3\text{-}C_2B_3H_6)Co(C_5H_5)$, IIa	CCl_4	+1.8 (121)[c]	
$(2,3\text{-}C_2B_3H_5)Co_2(C_5H_5)_2$, III	$CDCl_3$	−57.3 (135), −6.3 (148)	1, 2
$(2\text{-}CH_3\text{-}2,3\text{-}C_2B_3H_4)Co_2(C_5H_5)_2$, IIIa	$CHCl_3$	−53.2 (143), −7.0 (138)	1, 2
$(2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_3H_3)Co_2(C_5H_5)_2$, IIIb	$CDCl_3$	−50.4 (137), −9.0 (120)	1, 2
$(2,4\text{-}C_2B_3H_5)Co_2(C_5H_5)_2$, IV	CH_2Cl_2	−22.8 (149), −13.4 (155)	2, 1[b]
$[\sigma\text{-}5\text{-}(1\text{-}C_{10}H_7)\text{-}\pi\text{-}2,4\text{-}C_2B_4H_5]Co(C_5H_5)$, VI	CH_2Cl_2	−10.9 (153), −2.8,[d] −0.2 (166)	2, 1, 1
$(CH_3)_4N^+[(2,4\text{-}C_2B_4H_6)_2Co]^-$, VIII	$(CH_3)_2CO$	−2.3 (156), +6.1 (156)	3, 1
$(2,3\text{-}C_2B_4H_6)Ni[(C_6H_5)_2PCH_2]_2$, IX	C_6H_6	−17.1[e]	
$(C_2B_5H_7)Ni_2(C_5H_5)_2$, X	$CDCl_3$	−31.9 (157), −6.3 (170), +3.9 (170), +6.3 (177)	1, 1, 2, 1

[a] Chemical shifts relative to $BF_3 \cdot O(C_2H_5)_2$. [b] Estimated from overlapped doublets. [c] Asymmetric doublet, shoulder on downfield side. [d] Singlet assigned to *B*-naphthyl group. [e] Broad resonance, $w_{1/2} \approx 560$ Hz.

Table II. 100-MHz ^1H Nmr Data

		δ,[a] ppm (J, Hz)			
Compd	Solvent	C_5H_5	Cage CH	Other	Rel Areas
I	CCl_4	−5.08	−5.96		5, 2
Ia	CCl_4	−4.72	−5.33 (4)[b]	−2.35 (CH_3)	5, 1, 3
Ib	CCl_4	−4.52		−2.11 (CH_3)	5, 6
II	CCl_4	−5.44	−5.44	−3.63 (173),[c] +6.95[d]	~7, 3, 2[e]
IIa	$CDCl_3$	−4.80	−4.63	−1.89 (CH_3), +6.0[d]	5, 1, 3, 2[e]
III	$CDCl_3$	−4.42	−5.52		10, 2
IIIa	CCl_4	−4.35	−5.19 (3)[b]	−2.74 (CH_3)	10, 1, 3
IIIb	$CDCl_3$	−4.33		−2.55 (CH_3)	10, 6
IV	CCl_4	−4.48	−2.40[f]		10, 2
VI	CCl_4	−4.69	−4.01 (4)[b]	−8.56,[g] −7.74,[g] −7.34[g]	5, 1, 1, 3, 3
			−3.92 (4)[h]		1
VIII	$(CD_3)_2CO$		~−3.3[i]	−3.28[i]	
IX	$CDCl_3$		−4.85	−7.40,[j] −2.05 (18.5)[k]	1, 10, 2
X	$CDCl_3$	−5.30	−2.79		10, 2

[a] Chemical shifts relative to $(CH_3)_4Si$. Except where otherwise indicated, H−^{11}B quartets were weak and/or masked by H–C resonances. [b] Doublet attributed to H–B–C–H proton–proton coupling. [c] Terminal H−^{11}B quartet. [d] H_{bridge} resonance. [e] Estimated from overlapping peaks. [f] Singlet with unresolved triplet-like fine structure. [g] Center of multiplet; naphthyl peaks. [h] Triplet attributed to H–B–C–H proton–proton coupling. [i] Sharp $(CH_3)_4N^+$ singlet, with shoulder on low-field side attributed to cage H–C resonance. [j] Most intense peak of multiplet; phenyl resonance. [k] Doublet; methylene resonance.

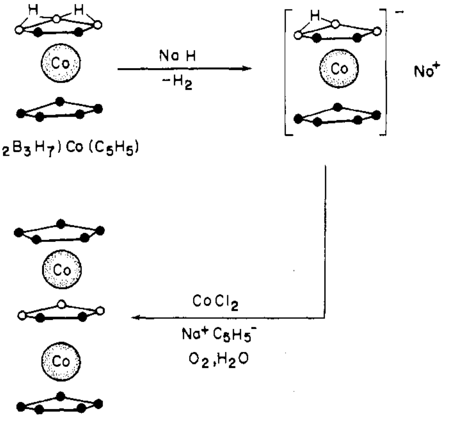

Figure 3. Reaction scheme for the synthesis of $(2,3\text{-}C_2B_3H_5)Co_2(C_5H_5)_2$ from $(C_2B_3H_7)Co(C_5H_5)$ *via* the $(C_2B_3H_6)Co(C_5H_5)^-$ ion.

ethereal solvent to generate an open-cage anionic intermediate which can undergo metal ion insertion has been thoroughly studied by Hawthorne[8-10] and applied to a variety of closo carboranes having eight to twelve vertices. Frequently the procedure results in polyhedral expansion,[8] *i.e.*, the enlargement of the original cage system by incorporation of a metal atom, but in the study of $2,4\text{-}C_2B_5H_7$ by Miller and Grimes[1] the major product surprisingly was a "nonexpanded" cage, $(\pi\text{-}2,4\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$. While this particular result could have been a consequence of the treatment of the reaction products with aqueous acetone, a similar reaction of $C_2B_5H_7$ with sodium naphthalide, $FeCl_2$, and NaC_5H_5 and work-up in the *absence* of water also failed to give "expanded" products[5] (nearly all of the reported polyhedral expansion reactions have employed treatment with air or oxygen[8]). In view of these findings, it was of interest to examine the application of the sodium naphthalide–metal ion treatment to two remaining lower closo carboranes, $1,6\text{-}C_2B_4H_6$ and $1,5\text{-}C_2B_3H_5$, and also to the open-cage system $2,3\text{-}C_2B_4H_8$.

The reaction of $1,6\text{-}C_2B_4H_6$, a closed octahedral carborane having carbon atoms in nonadjacent vertices, with 2 molar equiv of sodium naphthalide followed by excess sodium cyclopentadienide and cobalt(II) chloride, work-up in aqueous acetone and exposure to air, and separation on silica gel tlc plates gave a series of three- and four-boron cobaltacarborane products in a total yield of ~6%. In a reaction of 22 hr at room temperature, the major product was the triple-decked species $(\pi\text{-}2,4\text{-}C_2B_3H_5)Co_2(\pi\text{-}C_5H_5)_2$ (IV, an isomer of III), with smaller amounts of $(\pi\text{-}C_2B_4H_6)Co_2(\pi\text{-}C_5H_5)_2$ (V, identical with a previously reported[1] product obtained from $2,4\text{-}C_2B_5H_7$), and a naphthyl derivative, $[\sigma\text{-}5\text{-}(1\text{-}C_{10}H_7)(\pi\text{-}2,4\text{-}C_2B_4H_5)]Co(\pi\text{-}C_5H_5)$ (VI). The reaction is shown schematically in Figure 4. Compound VI is isomeric, but not identical, with $[\sigma\text{-}3\text{-}(2\text{-}C_{10}H_7)(\pi\text{-}2,4\text{-}C_2B_4H_5)]Co(\pi\text{-}C_5H_5)$, obtained in the $C_2B_5H_7$ reaction[1] reported earlier. The fact that the naphthyl derivatives of $(\pi\text{-}2,4\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$ produced in the two reactions differ in two respects, *i.e.*, in the positions of cage attachment and of bonding to the naphthyl ring, implies significant differences in the mechanisms of formation of these species (it should be noted that only one

Table III. Infrared Absorptions (cm^{-1}; CCl_4 Solution *vs.* CCl_4)

$(2,3\text{-}C_2B_4H_6)Co(C_5H_5)$, I	3120 w, 3050 w, 2560 vs, 1825 w, 1765 w, 1700 w, 1680 w, 1420 m, 1265 m, 1185 m, 1110 m, 1030 sh, w, 1010 m, 980 w, 920 w, 870 m, 690 sh, m, 680 m, 610 w
$(2\text{-}CH_3\text{-}2,3\text{-}C_2B_4H_5)Co(C_5H_5)$, Ia	3940 w, 2115 w, 3030 w, 2975 w, 2950 w, 2920 m, 2860 m, 2555 vs, 1823 w, 1760 w, 1678 w, 1441 m, 1417 s, 1374 m, 1326 m, 1214 m, 1111 s, 1044 m, 1006 s, 958 m, 869 s, 827 s, 688 s
$[2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_4H_4]Co(C_5H_5)$, Ib	2976 m, 2943 m, 2909 s, 2857 m, 2549 vs, 1818 w, 1752 w, 1670 vw, b, 1452 sh, 1438 m, 1418 s, 1389 m, 1111 m, 1042 w, 1006 s, 909 m, 869 s, 849 sh, 838 s
$(2,3\text{-}C_2B_3H_7)Co(C_5H_5)$, II	3120 w, 3000 m, 2540 vs, 1870 m, 1820 m, 1750 w, 1635 m, 1550 m, 1415 m, 1340 w, 1110 m, 1050 m, 1005 m, 978 w, sh, 880 m, 865 sh, w, 700 sh, w, 680 w, 610 w
$(2\text{-}CH_3\text{-}2,3\text{-}C_2B_3H_6)Co(C_5H_5)$, IIa	3945 w, 3115 w, 2985 m, 2960 m, 2935 m, 2905 m, 2855 m, 2535 vs, 1870 s, 1817 m, 1747 w, 1628 m, 1553 s, 1445 m, 1417 m, 1379 m, 1367 m, 1114 m, 1097 w, 1080 s, 1005 s, 950 s, 921 m, 884 s, 826 s, 685 w
$(2,3\text{-}C_2B_3H_5)Co_2(C_5H_5)_2$, III[a]	3110 w, 2990 m, 2500 s, 1815 w, 1740 sh, w, 1720 w, 1600 w, 1415 w, 1265 w, 1110 m, 1100 sh, w, 1005 m, 940 w, 860 sh, w, 830 w
$(2\text{-}CH_3\text{-}2,3\text{-}C_2B_3H_4)Co_2(C_5H_5)_2$, IIIa	3940 w, 3105 w, 2980 m, 2910 m, 2850 m, 2500 vs, 1804 w, 1739 w, 1670 w, 1650 sh, 1418 s, 1365 m, 1308 m, 1200 w, 1111 s, 1003 s, 905 m, sh, 880 m, sh, 860 m, sh
$[2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_3H_3]Co_2(C_5H_5)_2$, IIIb[a]	2992 s, 2910 m, 2852 m, 2494 vs, 1809 w, 1742 w, 1667 w, broad, 1417 m, 1371 w, 1362 w, 1220 w, b, 1111 m, 1007 s, 881 w, 841 w
$(2,4\text{-}C_2B_3H_5)Co_2(C_5H_5)_2$, IV[b]	2995 w, 2504 vs, 2400 w, sh, 1814 w, 1601 w, 1410 w, 1110 s, 1007 m, 947 m, 927 w
$[\sigma\text{-}5\text{-}(1\text{-}C_{10}H_7)\text{-}\pi\text{-}2,4\text{-}(C_2B_4H_5)]Co(C_5H_5)$, VI[b]	3065 w, sh, 3040 m, 2955 m, 2925 s, 2865 m, sh, 2572 vs, 1587 w, 1505 m, 1497 m, 1452 m, 1415 m, 1292 w, 1260 w, 1244 m, 1195 m, 1148 m, 1114 m, 1095 m, 1054 m, 1012 m, 925 w, 837 s, 800 s, 780 s, 660 w, 620 m
$[(CH_3)_4N][(2,4\text{-}C_2B_4H_6)_2Co]$, VIII[b]	2955 m, 2925 m, 2860 w, 2540 vs, 1710 w, 1465 w, 1375 w, 1168 m, 1055 m, 920 w, 872 m, 815 w
$(2,3\text{-}C_2B_4H_6)Ni[(C_6H_5)_2PCH_2]_2$, IX[b]	3020 w, 2980 w, 2920 w, 2535 vs, 1960 w, 1900 w, 1820 w, 1575 w, 1487 m, 1410 w, 1310 w, 1188 m, 1100 s, 1073 w, 1030 m, 1002 m, 965 w, 875 w, sh, 850 m, 818 m
$(C_2B_5H_7)Ni_2(C_5H_5)_2$, X	3110 w, 3000 w, 2545 s, 1800 w, 1730 w, 1600 w, 1450 w, 1130 m, 1100 m, 1050 m, 1020 m, 1000 m, sh, 960 w, 910 w, 870 w, 620 w

[a] CH_3Cl solution *vs.* CH_3Cl. [b] CH_2Cl_2 solution *vs.* CH_2Cl_2.

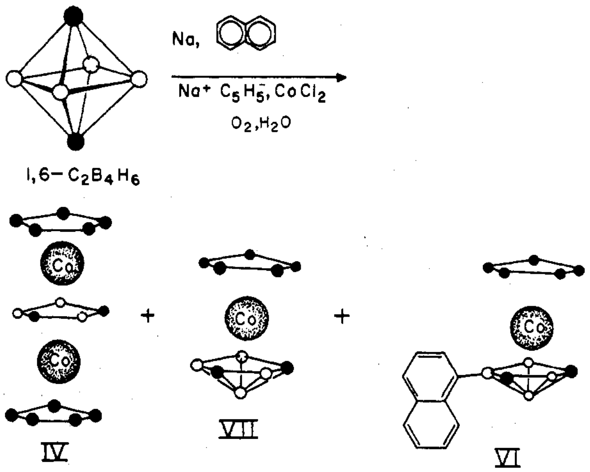

Figure 4. Reaction scheme for the synthesis of cobalt metallocarboranes from $1,6\text{-}C_2B_4H_6$, showing the proposed structures of IV, VI, and VII.

σ-naphthyl derivative was detected or isolated in each reaction). For example, it is possible that naphthylation occurs in one case prior to insertion of the metal atom into the cage and in the other case subsequent to it. However, this is one of many mechanistic aspects of these metallocarborane syntheses that have yet to be resolved.

The parent compound $(\pi\text{-}2,4\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$ (VII) was obtained only in trace quantity, in contrast to the $C_2B_5H_7$ reaction in which it was the predominant product.[1] Shorter reaction times with sodium naphthalide (7 hr) were found to favor the formation of VI and VII at the expense of IV, indicating that IV is formed from VII during prolonged reaction. These results are in some respects reminiscent of those obtained[1] with $2,4\text{-}C_2B_5H_7$, particularly in the formation of both mono- and dicobalt compounds and of σ-bonded naphthyl derivatives. However, the overall low yield of metallocarboranes from $C_2B_4H_6$ contrasts with a conversion of at least 25% from $C_2B_5H_7$.

This trend is further illustrated in the case of $1,5\text{-}C_2B_3H_5$, the least stable polyhedral carborane of the $C_2B_{n-2}H_n$ homologous series. When $1,5\text{-}C_2B_3H_5$ was subjected to the same conditions and work-up as $1,6\text{-}C_2B_4H_6$, a reaction clearly occurred but no metallocarboranes were obtained. The results of the application of the sodium naphthalide–metal insertion technique to $C_2B_4H_6$ and $C_2B_3H_5$ suggest that this method, which has proven extremely useful in the synthesis of metallocarboranes from large- and medium-sized carboranes,[8-10] may reach its practical lower limit of utility in the case of $C_2B_5H_7$.[1] As it happens, metallocarboranes have been prepared in good yield from $C_2B_4H_6$ and $C_2B_3H_5$ in gas-phase reactions,[6] indicating that an extensive metallocarborane chemistry derived from these systems is possible with the use of reaction conditions less severe than in the sodium naphthalide treatment.

The reaction of $2,3\text{-}C_2B_4H_8$ with sodium in the presence of naphthalene in THF resulted in considerable gas evolution, as expected for a nido carborane containing hydrogen bridges, and the solution turned yellow-orange. After 15 hr at 25° the solution was filtered under nitrogen and the red filtrate was combined with a solution of NaC_5H_5 in THF and added dropwise to a $CoCl_2$-THF slurry. Following filtration and solvent removal *in vacuo*, treatment with water in a stream of air, and extraction with methylene chloride, separation on a silica gel column gave the same products II and III (20 and 5% yield, respectively) as were obtained from $Na^+C_2B_4H_7^-$, described above; however, only a trace of I was isolated

(Figure 1). Thus, not surprisingly the syntheses of cobaltacarboranes from $C_2B_4H_8$ *via* the sodium hydride and sodium naphthalide routes follow much the same pathway except that the degradation of I to II is much more extensive in the presence of sodium naphthalide.

Attempted Preparation of the $(\pi\text{-}2,4\text{-}C_2B_4H_6)_2Co^-$ Anion. The synthesis of small metallocarboranes has thus far focused almost entirely on mixed-ligand species containing either a formal 2+ metal coordinated to a dinegative carboranyl ligand and a neutral ligand (*e.g.*, CO), or a formal 3+ metal bonded to a dinegative carboranyl ligand and a uninegative cyclopentadienide ring. In addition to the ease of preparation of these compounds, a primary advantage is their electrical neutrality, which greatly simplifies the task of isolation and characterization; for example, nearly all of the small cyclopentadienylcobaltacarboranes[1,2] prepared thus far are sufficiently volatile for analysis by mass spectroscopy. However, in conjunction with the work reported earlier on the synthesis of cobaltacarboranes[1] from $2,4\text{-}C_2B_5H_7$ *via* sodium naphthalide reduction, it was of interest to conduct this reaction in the absence of NaC_5H_5 to determine whether a bis(carboranyl)cobalt(III) species could be isolated (a number of bis(carboranyl) complexes of large carboranes have been reported[9,10,16]). Since the main product of the original reaction sequence[1] was $(\pi\text{-}2,4\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$, the principal species expected in the present case was $(\pi\text{-}2,4\text{-}C_2B_4H_6)_2Co^-$. Accordingly, $2,4\text{-}C_2B_5H_7$ was treated with sodium naphthalide in THF as described elsewhere[1] and the resulting solution was added, after filtration, to $CoCl_2$ in THF. After stirring the resulting dark brown solution overnight, removal of the solvent, extraction of the residue with water, and filtration, an orange solution was obtained, which on addition of tetramethylammonium chloride gave a golden precipitate presumed to be $(CH_3)_4N^+(\pi\text{-}2,4\text{-}C_2B_4H_6)_2Co^-$, VIII. The salt was purified by column chromatography, but in a yield too low for definitive characterization. The ^{11}B and ^1H nmr spectra are consistent with the assigned formula, and despite the nonvolatility of the salt at room temperature, a strong mass spectrum exhibiting a cutoff at *m/e* 208 and a characteristic eight-boron pattern[17] was obtained at 220° corresponding to the parent ion of the protonated species, $(C_2B_4H_6)_2CoH^+$ (attempts to isolate such an ion from solution have been unsuccessful[18,18a]). The mass spectrum contains no indication of significant decomposition or reaction other than protonation. Nevertheless, while the formulation of VIII from these data is probably correct, it cannot be regarded as definitive.

Nickel Metallocarboranes from $Na^+C_2B_4H_7^-$. The reaction of 1,2-bis(diphenylphosphino)ethanenickel(II) chloride with $Na^+C_2B_4H_7^-$ in THF produced brown needles of $(\pi\text{-}2,3\text{-}C_2B_4H_6)Ni[(C_6H_5)_2PCH_2]_2$, IX (Figure 5), which was characterized from spectroscopic data (Tables I-III) as described below.

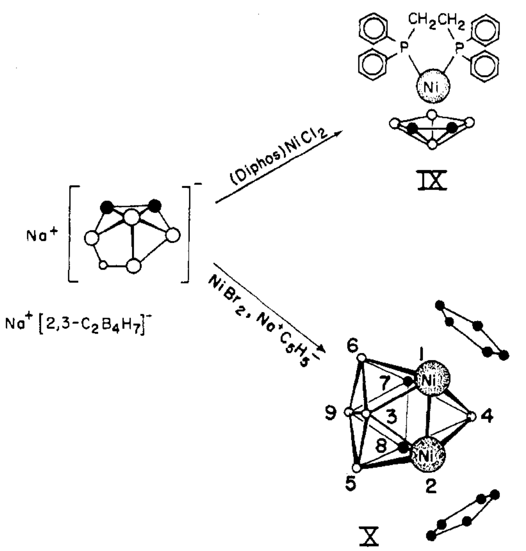

Figure 5. Reaction scheme for the synthesis of nickel metallocarboranes from $NaC_2B_4H_7$, showing the proposed structures of IX and X. The suggested structure of X is idealized based on a tricapped trigonal prism, but distortion is expected (see text). Diphos = bis(diphenylphosphino)ethane.

The slow addition of a THF solution of $Na^+C_5H_5^-$ and $Na^+C_2B_4H_7^-$ to anhydrous nickel(II) bromide in THF gave a dark green solution. On stirring 12 hr, removal of solvent *in vacuo*, and treatment with aqueous HCl under a stream of air, followed by extraction with methylene chloride and separation on silica gel, a small quantity of brown diamagnetic crystalline $C_2B_5H_7Ni_2(C_5H_5)_2$, X, was isolated. Although the yield was low, this compound is structurally interesting and is discussed in the following section.

A trace product of this reaction gave a mass spectrum corresponding to $(C_2B_7H_9)Ni_2(C_5H_5)_2$ but structural characterization was not possible from the weak ^{11}B and ^1H nmr spectra obtained.

Structural Characterization. The empirical formulas of the new compounds have been established from mass spectroscopic intensity profiles and exact mass measurements. The infrared spectra of all compounds (Table III) contain ligand CH, cage CH (~3100 cm^{-1}), and terminal BH (~2600 cm^{-1}) absorptions. The proposed structures are consistent with the ^{11}B and ^1H nmr spectra, and in most cases a unique or strongly favored structure can be assigned. It is assumed that the gross geometry for each polyhedral cage is the same as for other carborane species having the same number of vertices, *e.g.*, that seven-atom polyhedra are pentagonal bipyramidal as in the established structures $2,4\text{-}C_2B_5H_7$[19] and $CH_3GaC_2B_4H_6$.[11] Compounds V and VII are identical with previously reported metallocarboranes.[1]

$(\pi\text{-}2,3\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$, I. The ^{11}B nmr spectrum indicates a pair of equivalent boron atoms and two other borons in unique environments, and the ^1H nmr spectrum suggests equivalent cage CH groups. I is distinguished from its previously reported[1] isomer, $(\pi\text{-}2,4\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$, by their respective syntheses from $2,3\text{-}C_2B_4H_8$ and $2,4\text{-}C_2B_5H_7$ in which the carbon atoms are adjacent and nonadjacent, respectively. Other possible structures, in which the metal atom occupies an equatorial (four-coordinate vertex) location are inconsistent with the nmr data. The formal $2,3\text{-}C_2B_4H_6^{2-}$ ligand occurs in the established[11] structure of $CH_3GaC_2B_4H_6$. The ^{11}B nmr spectrum of the *C*-monomethyl derivative Ia is unremarkable, except for the fact that the expected CH_3-induced nonequivalence of the basal borons is not observed, a frequently noted effect in small metallocarborane spectra (see, for example, compound IIa below, and the structurally established parent species[13] $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$, whose spectrum[5] exhibits only one reso-

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(16) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

(17) J. F. Ditter, F. J. Gerhart, and R. E. Williams, *Advan. Chem. Ser.*, No. 72, 191 (1968).

(18) D. C. Beer and R. N. Grimes, unpublished results.

(18a) Note Added in Proof. The closely related species $(C_2B_4H_6)CoH(C_2B_3H_7)$ has recently been isolated in our laboratory: W. M. Maxwell and R. N. Grimes, to be submitted for publication.

(19) R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, 43, 2166 (1965).

nance). The ^{11}B nmr spectrum of the *C,C′*-dimethyl species Ib deserves comment since it consists of two apparent overlapped doublets of equal area. Such a spectrum can be reconciled with the proposed structure of I only if coincidental superposition of the resonances of B(5) and B(7) is assumed.[20] Since the spectra of I and Ia clearly reveal three different boron environments and since Ib was prepared from $Na^+[2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_4H_5]^-$ by a procedure identical with the syntheses of I and Ia, such an interpretation seems unavoidable. The resonances at δ −13 to −11 in the spectra of I, Ia, and Ib are probably those of B(5), which is not bonded to carbon and presumably is less affected by C-substitution than are B(1), B(4), and B(6).

$(\pi\text{-}2,3\text{-}C_2B_3H_7)Co(\pi\text{-}C_5H_5)$, II. The assigned cyclocarboranyl sandwich geometry (Figure 1) is supported by the ^{11}B and proton nmr spectra, which are similar to those of the structurally analogous compound $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$,[3,5,13] and by the facile conversion of II to the triple-decked sandwich III, described below. The spectroscopic data for the *C*-monomethyl derivative, IIa, are also consistent with the proposed structure; in both compounds, bridge protons are indicated by infrared absorptions near 1900 cm^{-1} and by broad proton nmr signals near δ +6 ppm relative to TMS.

$(\pi\text{-}2,3\text{-}C_2B_3H_5)Co_2(\pi\text{-}C_5H_5)_2$, III. The ^{11}B and ^1H nmr spectra of III, IIIa, and IIIb are consistent with the triple-decked structure in Figure 2, which has been established in an X-ray study of IIIa. The more interesting details of the solid-state structure of IIIa, described in an earlier communication,[2] include the approximate 5° tilt of each C_5H_5 ring toward B(5) and away from C(2)–C(3) and the fact that one C_5H_5 ring (C(11)–C(15)) is essentially eclipsed with respect to the central carboranyl ring while the other C_5H_5 ligand (C(21)–C(25)) is in a staggered configuration. Discussion of the significance of these findings will be prudently delayed until X-ray structures of additional compounds, especially the parent species III and IV, become available.

$(\pi\text{-}2,4\text{-}C_2B_3H_5)Co_2(\pi\text{-}C_5H_5)_2$, IV. The nmr data indicate equivalent $Co(C_5H_5)$ groups, equivalent cage carbon atoms, and two different boron environments in a 2:1 ratio, all of which are consistent with the triple-decked structure analogous to III, shown in Figure 4. Two alternative possibilities containing both cobalt atoms in four-coordinate equatorial positions in the pentagonal bipyramid, with the cage carbons in either equatorial or apical locations, are not eliminated by the nmr data but are considered unlikely since the relatively long Co–Co and/or Co–B bonds would produce a severely distorted and flattened cage.[21,22]

$\sigma\text{-}5\text{-}(1\text{-}C_{10}H_7)(\pi\text{-}2,4\text{-}C_2B_4H_5)Co(\pi\text{-}C_5H_5)$, VI. The ^{11}B nmr spectrum contains a singlet indicating attachment of the naphthyl ligand to a boron atom. Although the 2:1:1 pattern of resonances suggests that the equivalence of the equatorial borons B(5) and B(6) is retained, which would require substitution at B(3) or B(7), the ^1H nmr spectrum clearly reveals two CH resonances (each having fine structure attributed to H–B–C–H coupling[23]). This establishes ligand attachment at B(5) and indicates that the area 2 signal in the ^{11}B spectrum arises from coincidental superposition. The ^1H spectrum exhibits a pattern of naphthyl peaks closely resembling the spectrum of $1\text{-}NO_2C_{10}H_7$[24] and considerably different from those of $2\text{-}NO_2C_{10}H_7$[24] and $\sigma\text{-}3\text{-}(2\text{-}C_{10}H_7)(\pi\text{-}2,4\text{-}C_2B_4H_5)Co(\pi\text{-}C_5H_5)$,[1] indicating 1- rather than 2-naphthyl substitution.

$(CH_3)_4N^+[(\pi\text{-}2,4\text{-}C_2B_4H_6)_2Co]^-$, VIII. The ^{11}B nmr spectrum exhibits two resonances in a 3:1 area ratio[25] and is qualitatively very similar to that of the known[1] compound, $(\pi\text{-}2,4\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$. The spectrum clearly indicates that the two carboranyl ligands are symmetrically bound to the metal such that each boron in one cage is magnetically equivalent to its counterpart in the other. The ^1H nmr spectrum is essentially uninformative since the cage H–C resonance is nearly masked by the large $(CH_3)_4N^+$ peak.

$(\pi\text{-}2,3\text{-}C_2B_4H_6)Ni[(C_6H_5)_2PCH_2]_2$, IX. The ^{11}B nmr spectrum consists of a featureless hump and thus conveys no structural information, but the ^1H nmr spectrum conforms with the proposed structure, which is based primarily on the analogy with other C_2B_4M metallocarboranes (M = Fe,[3-5] Co,[1] Ga,[11] In[11]), in which the metal atom occupies a five-coordinate vertex in the pentagonal bipyramid. The single CH resonance indicates equivalent cage carbon atoms, which are assumed to occupy adjacent positions in view of the synthesis from the $2,3\text{-}C_2B_4H_7^-$ ion. The equivalence of the four phenyl groups and of the two methylene units is also evident from the spectrum.

$(\pi\text{-}C_2B_5H_7)Ni_2(\pi\text{-}C_5H_5)_2$, X. The normal gross geometry of closed nine-atom borane,[26] carborane,[27] and metallocarborane[10] polyhedra is that of a symmetrically tricapped trigonal prism. Compound X, however, is unusual in that it contains two more electrons than the analogous cobalt species $(\pi\text{-}C_2B_5H_7)Co_2(\pi\text{-}C_5H_5)_2$ which was prepared earlier.[1] The cobalt compound and its cage-isoelectronic analogs $C_2B_7H_9$[27] and $B_9H_9^{2-}$ [26] each contain 20 valence electrons in the polyhedral framework and thus satisfy the $2n + 2$ rule[22,28,29] for a closed nine-atom cage. Since compound X has 22 cage valence electrons, some type of distortion or opening of the tricapped trigonal prism is to be expected. However, X has no extra hydrogens to occupy bridging locations on an open face, and a nido metallocarborane cage having an open (square) face with no hydrogen bridges is unprecedented although not inconceivable.[30,31] A subtler distortion, which may for example take the form of a stretched nickel–nickel bond,[32] seems more likely. Hence the structure is presumed

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(20) Such superpositions, which occur frequently in metallocarborane ^{11}B nmr spectra, do not imply or require identical values of δ for the superimposed peaks, since apparent coalescence of two broad peaks into a single peak in these spectra can occur when the δ values are merely close, *e.g.*, within ~10 Hz.

(21) Metallocarboranes[6,8] and metalloboranes[22] containing metal atoms in probable four-coordinate vertices are known, but no such species containing two metals in the equator of a pentagonal bipyramid has been reported.

(22) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 95, 5078 (1973).

(23) Similar coupling has been noted earlier.[1,2] The fact that the cage CH resonances are a doublet and triplet, respectively, is consistent with the proposed structure of VI since one of the CH groups is adjacent to only one ring (equatorial) BH group, while the other CH has BH units on either side, giving rise to a triplet H–B–C–H coupling pattern. The coupling of the apex BH to the CH groups is assumed to be negligible, perhaps due to the large angle between the H–B bond and the plane of the C_2B_3 equatorial ring.

(24) P. R. Wells and P. G. E. Alcorn, *Aust. J. Chem.*, 16, 1108 (1963).

(25) Superposition[20] of two nonequivalent ^{11}B–H resonances is indicated by the observation of only two doublets, as discussed earlier[1] for $(\pi\text{-}2,4\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$.

(26) L. J. Guggenberger, *Inorg. Chem.*, 7, 2260 (1968).

(27) T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *Inorg. Chem.*, 7, 1076 (1968).

(28) (a) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 11, 1974 (1972); (b) K. Wade, *J. Chem. Soc. D*, 792 (1971); *Inorg. Nucl. Chem. Lett.*, 8, 823 (1972).

(29) (a) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 95, 7633 (1973); (b) C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 543 (1973).

(30) The only known and structurally established neutral boron cage compound having an open (nontriangular) face and lacking bridge hydrogens is $2,3,4,5\text{-}C_4B_2H_6$, a pentagonal pyramid.[31]

(31) R. A. Beaudet, *J. Chem. Soc., Chem. Commun.*, 928 (1973).

to retain the essential tricapped trigonal-prismatic geometry and the nmr data will be discussed on this basis. The ^{1}H nmr spectrum indicates equivalent Ni(C_5H_5) and CH groups, and the ^{11}B spectrum exhibits a 1:1:2:1 pattern suggesting that a pair of borons are in identical environments while the remaining boron atoms are unique. If the metal atoms are restricted to five-coordinate vertices, as discussed in an earlier paper,[1] and if the cage carbons are assumed to be adjacent[1,8] (considering the $C_2B_4H_7^-$ precursor), only two structures consistent with the nmr data are possible. One of these has the metal atoms in positions[33] 1 and 2 (Figure 5) and the cage carbons at 7 and 8, while in the other arrangement the nickels are in locations 1 and 7 and the carbon atoms at 2 and 8. The (1,2)-7,8 structure is slightly preferred in that it has a unique boron in a low-coordinate vertex [B(4)] adjacent to both metal atoms, which is consistent with the low-field ^{11}B nmr signal[34] of area 1; the alternative (1,7)-2,8 geometry would have two such boron atoms and is thus a less attractive possibility.

Compound X is analogous to the previously reported[1] species (π-(1,8)-5,6-$C_2B_5H_7$)Co_2(π-C_5H_5)$_2$ (formerly numbered (3,8)-1,9) which also incorporates a formal $M_2C_2B_5$ cage. It is of interest that each of the most probable structures of X has a direct nickel–nickel bond. Since the nmr spectra indicate that X is essentially diamagnetic despite the presence of formal nickel(III), spin pairing is evident which presumably would be facilitated by a direct metal–metal interaction, although pairing is known to occur in some cases even in the absence of metal–metal bonding.[35]

Experimental Section

Materials. 1,6-Dicarba-*closo*-hexaborane(6) ($C_2B_4H_6$), 2,4-dicarba-*closo*-heptaborane(7) ($C_2B_5H_7$), and 1,5-dicarba-*closo*-pentaborane(5) ($C_2B_3H_5$) were purchased from Chemical Systems, Inc., Irvine, Calif., and purified by glpc (30% Apiezon L on Chromosorb W at 35–45°). Solutions of sodium 2,3-dicarba-*nido*-hexaborate(1–) ($NaC_2B_4H_7$) in tetrahydrofuran were prepared from 2,3-$C_2B_4H_8$ as described elsewhere.[15,36] Anhydrous cobalt(II) chloride was obtained from $CoCl_2 \cdot 6H_2O$ (Baker) by dehydration *in vacuo* at 160°. All solvents were reagent grade, and tetrahydrofuran (THF) was dried over lithium aluminum hydride before use. Nickel(II) bromide (Alfa) and naphthalene (Fisher) were used as received. Solutions of sodium cyclopentadienide (NaC_5H_5) in THF were prepared from cyclopentadiene and sodium metal as described previously.[1] Dichloro-1,2-bis(diphenylphosphino)ethanenickel(II) was synthesized by the method of Booth and Chatt.[37] Cyclopentadiene was distilled from dicyclopentadiene (Aldrich).

Spectra. Boron-11 nmr spectra at 32.1 MHz and proton nmr spectra at 100 MHz were obtained on a Varian HA-100 nmr spectrometer. Infrared spectra were run in solution (*vs.* pure solvent) on a Beckman IR-8 instrument. Unit-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. High-resolution mass spectra were recorded on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source and interfaced to a PDP-8I computer. All high-resolution spectra were obtained under chemical ionizing conditions in argon–water as described in an earlier paper.[1]

Cobalt Metallocarboranes from $NaC_2B_4H_7$. A filtered solution of $NaC_2B_4H_7$ prepared from 5.06 mmol of $C_2B_4H_8$ and 6 mmol of NaH in THF was added to a filtered solution of NaC_5H_5 obtained from 19.6 mmol of C_5H_6 and 21.6 mmol of divided sodium in THF, and the combined solution was added dropwise over 20 min to a stirred solution of 25.1 mmol of anhydrous $CoCl_2$ in 50 ml of THF. The dark blue $CoCl_2$ solution immediately turned dark brown. After stirring for 12 hr at 25°, the solvent was distilled off under reduced pressure and the residue was suspended in 60 ml of H_2O and stirred for 2 hr under a stream of air. After filtration of the solution, the residue was extracted with methylene chloride followed by acetone. Thin-layer separation of the combined extracts on silica gel plates with CCl_4 gave orange (π-2,3-$C_2B_4H_6$)Co(π-C_5H_5), I [R_f 0.5, 104 mg (0.524 mmol, 10.3% yield), calcd mass 198.0562, found 198.0541], yellow (π-2,3-$C_2B_3H_7$)Co(π-C_5H_5), II [R_f 0.85, 156 mg (0.826 mmol, 16.3% yield), calcd mass 188.0547, found 188.0556], and red-brown (π-2,3-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$, III [R_f 0.25, 40 mg (0.129 mmol, 2.5% yield), calcd mass 310.0112, found 310.0115]. A trace of material having a mass spectroscopic cutoff at *m/e* 322, corresponding to ($C_2B_4H_6$)Co_2(C_5H_5)$_2$,[1] was also detected but the quantity was insufficient for further characterization.

Modification of the above procedure to include work-up in aqueous HCl gave substantially increased yields of I. In a typical experiment, 5 ml of a THF solution of 0.66 mmol of $NaC_2B_4H_7$ and 2.4 mmol of NaC_5H_5 was added to 2.96 mmol of $CoCl_2$ in THF and stirred for 2.5 hr at 25°, after which the solvent was removed at reduced pressure, 20 ml of 1 *M* HCl was added, and the solution was stirred for another 1 hr. Treatment with air, extraction with solvents, and tlc separation as described above gave 83 mg (0.42 mmol, 63% yield) of I, 5 mg (0.027 mmol, 4% yield) of II, and 4 mg (0.012 mmol, 2% yield) of III.

***C*-Monomethyl Cobalt Metallocarboranes from $NaCH_3C_2B_4H_6$.** A filtered solution of $Na^+CH_3C_2B_4H_6^-$, prepared by adding 12.3 mmol of NaH to 5.65 mmol of 2-CH_3-2,3-$C_2B_4H_7$[38] in 10 ml of THF, was combined with a filtered solution of $Na^+C_5H_5^-$ obtained from 21.6 mmol of C_5H_6 and 20.7 mmol of sodium in 15 ml of THF. The mixture was added dropwise over 40 min to a solution of 19.5 mmol of anhydrous $CoCl_2$ in 40 ml of THF and then was stirred for 20 hr at room temperature. Following the addition of 100 ml of H_2O and 10 ml of acetone, the resulting suspension was stirred under a stream of air for 2.5 hr and filtered, and the residue was extracted with acetone. Separation of the extract *via* column chromatography and tlc gave 0.538 g (2.54 mmol, 45% yield) of (π-2-CH_3-2,3-$C_2B_4H_5$)Co(π-C_5H_5), Ia, 114 mg (0.57 mmol, 10% yield) of (π-2-CH_3-2,3-$C_2B_3H_6$)Co(π-C_5H_5), IIa, and 54.8 mg (0.17 mmol, 3% yield) of (π-2-CH_3-2,3-$C_2B_3H_4$)Co_2(π-C_5H_5)$_2$, IIIa. The unit-resolution mass spectroscopic cutoffs of Ia, IIa, and IIIa are at *m/e* 212, 202, and 324, respectively, and the intensity profiles in the parent regions correspond respectively to four-, three-, and three-boron species (hydrogen abstraction is extensive in the spectrum of IIa, as well as in the parent compound II, but is not significant in the spectra of the other cobalt species).

***C,C'*-Dimethyl Cobalt Metallocarboranes from $Na(CH_3)_2C_2B_4H_5$.** The above procedure was repeated using a THF solution of $Na^+(CH_3)_2C_2B_4H_5^-$ prepared from 4.89 mmol of 2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$[38] and 7.4 mmol of NaH, a THF solution of $Na^+C_5H_5^-$ obtained from 19.2 mmol of C_5H_6 and 35.3 mg-atoms of sodium, and a solution of 30.0 mmol of $CoCl_2$ in THF. The reaction mixture was stirred for 16 hr and worked up as described in the preceding experiment, except that 1 *M* aqueous HCl was used in place of neutral H_2O. The isolated products were [π-2,3-$(CH_3)_2$-2,3-$C_2B_4H_4$]Co(π-C_5H_5), Ib [688 mg (3.29 mmol, 68% yield)], and [π-2,3-$(CH_3)_2$-2,3-$C_2B_3H_3$]Co_2(π-C_5H_5)$_2$, IIIb [5.1 mg (0.015 mmol, 0.3% yield)]. The expected product [π-2,3-$(CH_3)_2$-2,3-$C_2B_3H_5$]Co(π-C_5H_5), the dimethyl derivative of II, was detected in trace quantity from mass spectra (cutoff at *m/e* 216) but was not isolated. The mass spectra of Ib and IIIb exhibited cutoffs at *m/e* 226 and 338, respectively, and the parent-region profiles corresponded respectively to four- and three-boron patterns.

Bridge Deprotonation of (π-$C_2B_3H_7$)Co(π-C_5H_5). A solution of 34 mg (0.18 mmol) of the metallocarborane and 24 mg (0.98 mmol) of NaH in 7 ml of dry THF was frozen at –196° in an evacuated Pyrex reactor attached to a calibrated mercury manometer. The reaction mixture was warmed to room temperature and vigorous evolution of gas (H_2) ensued. After 22 min, 0.175 mmol of H_2 (corrected for THF vapor pressure) had accumulated, and after 1 hr of reaction 0.194 mmol had formed, corresponding to 107% of theory based on the reaction

$$(\mathrm{C_2B_3H_7})\mathrm{Co}(\mathrm{C_5H_5}) + \mathrm{NaH} \rightarrow \mathrm{Na^+(C_2B_3H_6)Co(C_5H_5)^-} + \mathrm{H_2}$$

The orange-brown solution was filtered, the solvent was removed by

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(32) Placement of the two "extra" electrons in a nickel–nickel antibonding orbital would be expected to lengthen the Ni–Ni bond.

(33) This discussion ignores enantiomers and equivalent structures. The numbering is consistent with the IUPAC system, presented in *Pure Appl. Chem.*, 683 (1972).

(34) A correlation between low-field ^{11}B nmr resonances and low-coordinate boron atoms adjacent to metal atoms in metallocarborane polyhedra has been empirically postulated.[1,8]

(35) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Interscience, New York, N. Y., 1973, p 549.

(36) M. L. Thompson and R. N. Grimes, *Inorg. Chem.*, 11, 1925 (1972).

(37) G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965).

(38) T. P. Onak, R. B. Drake, and G. B. Dunks, *Inorg. Chem.*, 3, 1686 (1964).

distillation *in vacuo*, and the solid was exposed to excess anhydrous HCl. After 1 hr, 25.7 mg (0.137 mmol) of pale yellow crystalline (π-$C_2B_3H_7$)Co(π-C_5H_5), II, was recovered (identified from comparison of ir and mass spectra with those of authentic material), corresponding to 76% of theory.

A separate experiment conducted identically, except for the substitution of DCl in place of HCl, gave (π-$C_2B_3H_6D$)Co(π-C_5H_5) identified from its mass spectroscopic cutoff at *m/e* 189. No species containing more than one D atom per molecule was detected.

Preparation of (π-2,3-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$ from Na^+[(π-2,3-$C_2B_3H_6$)Co(π-C_5H_5)]$^-$. The metallocarborane (π-$C_2B_3H_7$)Co(π-C_5H_5), II (52.2 mg, 0.278 mmol) was distilled *in vacuo* into a reactor at −196° containing 0.81 mmol of NaH in 5 ml of THF. On warming to 25°, vigorous gas evolution began and continued for ~15 min, during which the color of the solution changed from yellow to dark orange. To this solution was added a solution of NaC_5H_5 (1.04 mmol in 5 ml of THF), and the mixture was filtered in a glove box under N_2. The combined solution was added dropwise over 10 min to a stirred solution of 1.98 mmol of anhydrous $CoCl_2$ in 5 ml of THF under N_2. The solution immediately turned dark brown. After stirring for 12 hr at 25° the THF was distilled off under reduced pressure. The residue was suspended in 10 ml of H_2O and allowed to stir for 2 hr under a stream of air, followed by filtration, extraction of the solid with methylene chloride, and tlc separation. The only products obtained were (π-2,3-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$, III [13.8 mg (0.0445 mmol, 16% of theory)], identified from its ir and mass spectra by comparison with authentic III, and a trace of the starting material, II.

Cobalt Metallocarboranes from *closo*-1,6-$C_2B_4H_6$. In a typical experiment, 20 mmol of C_5H_6 was distilled *in vacuo* into a 100-ml flask containing 20 mg-atoms of finely divided sodium in 20 ml of THF, and the mixture was stirred at room temperature for 4 hr during which all of the sodium was consumed. 1,6-$C_2B_4H_6$ (5.0 mmol) was distilled *in vacuo* into a separate 100-ml flask containing 10 mmol of sodium and 10 mmol of naphthalene in 25 ml of THF, and the mixture was stirred at −78° for 30 min. The reaction vessel was slowly warmed to 0° over a period of 2 hr. The mixture was then warmed to 26° and stirred for an additional 20 hr. During the course of the reaction a color change from green to yellow-brown was noted. The carborane and NaC_5H_5 solutions were transferred into a drybox and added with mixing to a pressure-equalized addition funnel. The addition funnel was fitted to a 100-ml two-neck flask containing 7.5 mmol of anhydrous $CoCl_2$ in 20 ml THF and the solution was added dropwise over 2 hr. The $CoCl_2$ solution darkened and gas evolved as the addition was made. The reaction was stirred for 20 hr at 26° under a nitrogen atmosphere, after which the THF was stripped off under an aspirator vacuum. The resulting dark solid was dissolved in acetone and stirred in air for 1 hr. This acetone-soluble fraction dried to a dark gummy substance and was subsequently extracted with methylene chloride. The solution was concentrated and applied to a 2.25 cm × 50 cm liquid phase chromatographic column packed with 70–230 mesh silica gel and eluted with hexane. Six 15–20-ml fractions were collected and solvent was removed.

The resulting residue was applied to several tlc plates and eluted with CH_2Cl_2. A fast-moving yellow-green band and a slower moving yellow band were collected and extracted with CH_2Cl_2. The yellow-green band was identified from its mass spectrum and ^{11}B nmr spectrum as the previously reported[1] material, [π-(3,4)-1,7-$C_2B_4H_6$]Co_2(π-C_5H_5)$_2$ [1 mg (0.0031 mmol, 0.06%)]. The yellow band was characterized as [σ-5-(1-$C_{10}H_7$)-π-2,4-$C_2B_4H_5$]Co(π-C_5H_5), VI [5 mg (0.016 mmol, 0.32%); mass spectroscopic cutoff at *m/e* 324, corresponding to the $^{12}C_{17}{}^{11}B_4{}^{1}H_{17}{}^{59}Co^+$ parent ion].

The chromatographic column was then eluted with a 50:50 hexane–methylene chloride mixture and dark green (π-2,4-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$, IV, was collected. This compound was further purified by thin-layer chromatography with CCl_4 and recrystallized from a methylene chloride solution to give 62 mg (4%) of dark green crystals; calcd mass 310.0112, found 310.0138.

An experiment with excess $CoCl_2$ in which the sodium naphthalide–1,6-$C_2B_4H_6$ reaction was conducted over a shorter (7 hr) period gave 22 mg (1.2%) of VI and 6 mg (0.7%) of the known[1] parent compound (π-2,4-$C_2B_4H_6$)Co(π-C_5H_5), VII, which was identified from its ^{11}B nmr and mass spectra. Only a trace of IV was detected from mass spectroscopic evidence.

Cobalt Metallocarboranes from 2,3-$C_2B_4H_8$ *via* Sodium Naphthalide Reduction. Sodium metal (6.0 mmol) and a catalytic amount of naphthalene were added to a Schlenk tube under a nitrogen atmosphere. The tube was transferred to a vacuum line and 3.0 mmol of $C_2B_4H_8$ and 20 ml of THF were added. The mixture was allowed to stir at room temperature for 15 hr. During this time a large amount of gas evolved and the solution acquired a yellow-orange hue. The carborane solution was taken into a glove bag and filtered to give a white insoluble material and a red filtrate, which was mixed with a solution of 12.0 mmol of NaC_5H_5 in THF, added to a pressure-equalized addition funnel, and added dropwise over a 20 min period to a slurry of 8.0 mmol of $CoCl_2$ in THF. After a 12 hr reaction period the solution was filtered and the solvent was removed *in vacuo*. Water was added to the reaction flask and the contents treated for 1.5 hr under a stream of air. Filtration yielded a yellow filtrate and a dark gummy water-insoluble material. The dark solids were extracted with methylene chloride, and the extract was concentrated and applied to a silica gel column. Elution with hexane gave yellow (π-2,3-$C_2B_3H_7$)Co(π-C_5H_5), II (113 mg, 20% yield), identified from its ^{11}B nmr and mass spectrum by comparison with authentic II, and a trace of orange (π-2,3-$C_2B_4H_6$)Co(π-C_5H_5), I, identified from its mass spectrum, color, and R_f value. Elution with 50:50 hexane–methylene chloride gave red (π-2,3-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$, III (46 mg, 5%), identified from its ^{11}B nmr and mass spectra by comparison with those of the authentic compound.

Preparation of $(CH_3)_4N^+$[(π-2,4-$C_2B_4H_6$)$_2$Co]$^-$, VIII. 2,4-$C_2B_5H_7$ (5.0 mmol) was distilled *in vacuo* into a 100-ml reactor containing 10 mmol of sodium and 10 mmol of naphthalene in 25 ml of THF. The mixture was allowed to stir for 8–9 hr, during which an orange color developed. The solution was transferred to a 50-ml pressure-equalized addition funnel (which had been purged and filled with nitrogen). The addition funnel was then connected to a 250-ml round-bottom three-neck flask containing 5.0 mmol of anhydrous $CoCl_2$. As the addition was made, the $CoCl_2$:THF slurry changed from blue-green to dark brown. The mixture was stirred overnight at 26° under a nitrogen atmosphere. After removal of solvent, the black residue was extracted with water for 12 hr. The aqueous layer was then decanted and filtered to give an orange filtrate. Treatment of this solution with aqueous solution of tetramethylammonium chloride gave a cream-colored precipitate which was removed by filtration. After drying, this material was dissolved in methylene chloride and passed through a liquid-phase silica gel column using 50:50 methylene chloride–ethyl acetate as the eluent. The fast-moving yellow-gold band was collected and solvent removed. Further purification was effected using thin-layer chromatography with methylene chloride and ethyl acetate to give 12 mg of golden $(CH_3)_4N^+$[(π-2,4-$C_2B_4H_6$)$_2$Co]$^-$, VIII.

(π-2,3-$C_2B_4H_6$)Ni[$(C_6H_5)_2PCH_2$]$_2$, IX. A solution of 3.0 mmol of $Na^+C_2B_4H_7^-$ in 20 ml of THF was taken into a drybox, filtered, and transferred to a pressure-equalized addition funnel. The carborane solution was added dropwise under nitrogen to a solution of 1.5 mmol of [$(C_6H_5)_2PCH_2$]$_2$$NiCl_2$ in 20 ml of THF. The mixture was stirred at 26° for 12 hr. The resulting brown-violet solution was filtered, solvent was removed *in vacuo*, and the brown residue was transferred to a nitrogen glove bag and extracted with benzene. After removal of benzene *in vacuo*, the brown material was dissolved in a minimum of methylene chloride and cooled to 5° for 14 hr to form 100 mg of brown needle crystals. A second crop of crystals was obtained in the same manner from the mother liquor to give a total of 135 mg of IX (0.255 mmol, 17% yield); calcd mass for $^{12}C_{28}{}^{11}B_4{}^{31}P_2{}^{58}Ni{}^{1}H_{30}{}^+$ 530.1545, found 530.1533.

(π-$C_2B_5H_7$)Ni_2(π-C_5H_5)$_2$, X. THF solutions of $Na^+C_5H_5^-$ (15.8 mmol/20 ml) and $Na^+C_2B_4H_7^-$ (3.68 mmol/20 ml) were combined and added dropwise under nitrogen to a stirred solution of 23 mmol of anhydrous $NiBr_2$ in 50 ml of THF. The solution immediately turned dark green. After stirring for 12 hr at 25°, the solvent was removed *in vacuo*, and the residue was suspended in 50 ml of 1 *M* HCl and stirred for 2 hr under a stream of air. The solid was filtered off and extracted with methylene chloride. Tlc separation on silica gel with hexane gave 10 mg (0.030 mmol, 1% yield) of brown X; calcd mass for $^{12}C_{12}{}^{11}B_5{}^{58}Ni_2{}^{1}H_{17}{}^+$ 332.0500, found 332.0493.

A second tlc band contained a trace product which gave a mass spectrum consistent with a B_7Ni_2 species with a cutoff at *m/e* 356 corresponding to ($C_2B_7H_9$)Ni_2(C_5H_5)$_2$, a ^1H nmr signal at δ −5.3 (relative to $(CH_3)_4Si$) attributed to C_5H_5 protons, and a ^{11}B nmr spectrum containing one clearly distinguishable doublet at δ −60 (relative to $BF_3 \cdot O(C_2H_5)_2$) with several broad overlapped resonances at higher field.

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Registry No. I, 50860-25-8; Ia, 50978-01-3; Ib, 50932-66-6; II, 50860-26-9; IIa, 50860-27-0; III, 39388-45-9; IIIa, 39388-46-0; IIIb, 51108-06-6; IV, 39388-44-8; VI, 50860-28-1; VIII, 51108-04-

4; IX, 50860-29-2; X, 51108-05-5; *closo*-1,6-$C_2B_4H_6$, 20693-67-8; 2,3-$C_2B_4H_8$, 21445-77-2; 2,4-$C_2B_5H_7$, 20693-69-0; $[(C_6H_5)_2PCH_2]_2NiCl_2$, 14647-23-5; $CH_3C_2B_4H_7$, 34228-46-1; $(CH_3)_2C_2B_4H_6$, 20741-68-8.

Contribution from the Department of Chemistry,
Drexel University, Philadelphia, Pennsylvania 19104

2-, 3-, and 4-Picoline *N*-Oxide Complexes with Cobalt(II), Nickel(II), and Copper(II) Nitrates[1]

N. M. KARAYANNIS,* C. M. MIKULSKI, L. L. PYTLEWSKI, and M. M. LABES

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Complexes of 2-, 3-, and 4-picoline *N*-oxides (picO) with cobalt(II), nickel(II), and copper(II) nitrates were prepared, by utilizing either 2:1 or 8:1 ligand to metal salt ratios during the synthetic procedure. Characterization studies of these complexes led to the following formulations: (a) complexes prepared by using 2:1 L to M ratios, $[M(2\text{-picO})_2(ONO_2)(O_2NO)]$ (M = Co, Ni), $[Cu(2\text{-picO})_2(ONO_2)_2]$, $[Co(3\text{-picO})_2(O_2NO)_2]$, $[Ni(L)_2(O_2NO)_2]$ (L = 3- or 4-picO), $[Cu(L)(O_2NO)_2]$ (L = 3- or 4-picO); for $Co(NO_3)_2\cdot(4\text{-picO})$ a binuclear structure of the type $[(ONO_2)_2Co(4\text{-picO})_2Co(O_2NO)_2]$ is considered as possible; (b) complexes prepared by using 8:1 L to M ratios, $[M(2\text{-picO})_4(ONO_2)](NO_3)$ (M = Co, Ni), $[Cu(2\text{-picO})_4](NO_3)_2$, $[Co(L)_6](NO_3)_2$ (L = 3- or 4-picO), $[Ni(4\text{-picO})_6](NO_3)_2$, $[Ni(3\text{-picO})_5(ONO_2)](NO_3)$, $[Cu(4\text{-picO})_4(ONO_2)](NO_3)$; finally, for $Cu(NO_3)_2\cdot4(3\text{-picO})$ the overall evidence is compatible with either a monomeric ($[Cu(3\text{-picO})_4](NO_3)_2$) or a binuclear ($[(3\text{-picO})_3Cu(3\text{-picO})_2Cu(3\text{-picO})_3](NO_3)_4$) structure.

Introduction

A variety of 3d metal nitrate complexes with pyridine *N*-oxide (pyO) and its substituted derivatives were reported in recent years.[2-11] pyO forms complexes of the following types with divalent 3d metal nitrates: $M(pyO)_2(NO_3)_2$ (M = Mn–Zn), $Cu(pyO)_4(NO_3)_2$, $M(pyO)_6(NO_3)_2$ (M = Mn, Co, Ni, Zn).[4] The 2:1 complexes are neutral, involving coordination of both NO_3 groups, while the 4:1 Cu(II) complex and the 6:1 M(II) complexes are cationic and involve exclusively ionic nitrate.[2-4] The presence of substituents on the pyridine ring may introduce steric effects and influence the nature of substituted pyridine *N*-oxide–metal nitrate complexes as well as the highest possible ligand-to-metal ratio attained. An extreme case was recently observed with 2,6-lutidine *N*-oxide (2,6-lutO), which yields only 2:1 complexes with $M(NO_3)_2$ (M = Mn, Co, Ni, Cu, Zn), regardless of the amounts of ligand utilized during the synthetic procedure.[8] $Cu(2,6\text{-lutO})_2(NO_3)_2$ involves monodentate nitrato ligands, while the $M(2,6\text{-lutO})_2(NO_3)_2$ (M = Mn, Co, Ni, Zn) complexes are pentacoordinated, containing one mono- and one bidentate coordinated nitrate.[8] Several divalent 3d metal nitrate–aromatic amine *N*-oxide complexes with unusual stoichiometries have also been reported in the literature, *i.e.*, $Co(NO_3)_2\cdot3L$ (L = 4-ethoxypyridine *N*-oxide),[6] $Ni(NO_3)_2\cdot4L$ (L = 2-ethylpyridine *N*-oxide), $Ni(NO_3)_2\cdot4L$ (L = 2,4-lutidine *N*-oxide), and $Ni(NO_3)_2\cdot3L\cdot0.5H_2O$ (L = quinoline *N*-oxide).[5] It was of interest to us to investigate the nature of divalent 3d metal nitrate complexes with 2-, 3-, and 4-picoline *N*-oxides (2-, 3-, and 4-picO, respectively). The present paper reports on the synthesis and characterization of cobalt(II), nickel(II), and copper(II) nitrate complexes with these ligands.

Experimental Section

Chemicals. The picoline *N*-oxides were obtained commercially (Aldrich or Baker products) and utilized without further purification. Reagent grade hydrated metal nitrates, triethyl orthoformate, and organic solvents were used.

Synthetic Procedure. During a series of experiments ligand and metal salt were mixed in 2:1 molar ratio, and during another in 8:1 molar ratio. The following synthetic procedure was employed in both cases. A 0.5–1-g sample of the hydrated metal salt was dissolved in *ca.* 50 ml of a 15:1 (v/v) mixture of triethyl orthoformate (a dehydrating agent[12])–acetone. The resulting solution was warmed at 50–60° for *ca.* 30 min, under stirring, and a 5% (w/w) solution of the ligand in triethyl orthoformate was subsequently added (ligand to metal molar ratio 2:1 or 8:1). The reaction mixture was stirred at 50–60° for 15 min, a large excess of ligroin (bp 63–75°) was then added, and the mixture was allowed to cool slowly, under continuous stirring, which is continued at room temperature for another 2–3 hr. During this period gradual precipitation of the $M(NO_3)_2$–picO complexes occurred. The complexes were then filtered, thoroughly washed with ligroin, and dried in an evacuated desiccator over phosphorus pentoxide. As shown in Table I, which gives analytical data (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.), complexes of the following stoichiometries were obtained during this work. Interaction of ligand and salt in 2:1 molar ratio yielded 2:1 complexes in most cases with the following exceptions: the $Co(NO_3)_2$–4-picO and $Cu(NO_3)_2$–3- or –4-picO interactions led to the formation of 1:1 complexes. On the other hand, interaction of ligand and salt in 8:1 molar ratio led to the formation of the following products: 6:1 complexes in the cases of 3- or 4-picO–$Co(NO_3)_2$ and 4-picO–$Ni(NO_3)_2$; a 5:1 complex between 3-picO and $Ni(NO_3)_2$; and 4:1 complexes in all other cases.

Spectral, Magnetic, and Conductance Studies. Infrared (Tables II and III, Figures 1 and 2) and electronic (Table IV, Figures 3 and 4) spectra and magnetic susceptibility and conductance measurements

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