to regenerate the spectrum of the aquo complex.

The *N-d,l* complex, either as the blue solid or the orange species, is soluble and stable in 70% $HClO_4$ and concentrated H_2SO_4. Only the blue species is detectable in these solvents (Figure 3). The nmr spectrum of the complex in concentrated H_2SO_4 is similar to that of the *N-d,l* complex in D_2O although broadened by viscosity effects. The meso complex is insoluble in $HClO_4$ but dissolves in H_2SO_4 giving the spectrum indicated in Figure 3. The conversion between blue and orange species appears to be completely reversible, the solutions in concentrated H_2SO_4 and concentrated $HClO_4$ appear to obey Beer's law, and we believe the blue species is a five-coordinate cobalt(III) complex.

We have found that the $Co^{III}(N_4)(L)CH_3$ complexes are reduced at only very negative potentials. The cyclic voltammograms of $Co^{III}(Me_6[14]dieneN_4)(L)CH_3$ in acetonitrile were irreversible in that they exhibited no anodic wave; this may be due to rapid solvolysis of the axially distorted $Co^{II}(N_4)(L)CH_3$ products. Values of the half-wave potential (in CH_3CN *vs.* sce) were found to be $E_{1/2} = -1.3, -1.4$, and -1.8 V for $L = H_2O$, NCS^-, and CN^-, respectively.

Registry No. $[Co([14]aneN_4)(H_2O)CH_3](ClO_4)_2$, 51240-13-2; $[Co(Me_6[14]aneN_4)(H_2O)CH_3](ClO_4)_2$, 40489-13-2; $[Co(Me_6[14]dieneN_4)(H_2O)CH_3](ClO_4)_2$, 51240-15-4; $[Co(Me_6[14]dieneN_4)(CN)CH_3]ClO_4$, 51240-17-6; $[Co(Me_6[14]dieneN_4)(SCN)CH_3]ClO_4$, 51240-19-8; $[Co(Me_6[14]dieneN_4)(H_2O)(C_2H_3)](ClO_4)_2$, 51240-21-2; $Co(NH_3)_5O_2CCH_3{}^{2+}$, 16632-78-3; $Co(NH_3)_5O_2CCHCH_2{}^{2+}$, 44982-34-5; $Co(Me_6[14]dieneN_4)(OH_2)_2{}^{2+}$, 38331-68-9; $Co(Me_6[14]aneN_4)(OH_2)_2{}^{2+}$, 39162-58-8; $Co([14]aneN_4)(CH_3)(H_2O)^{2+}$, 51240-12-1; $Co(Me_6[14]aneN_4)(CH_3)(H_2O)^{2+}$, 47247-32-5; Co(*N-meso*-$Me_6[14]dieneN_4)(CH_3)(H_2O)^{2+}$, 51240-22-3; Co(*N-meso*-$Me_6[14]dieneN_4)(CH_3)(NCS)^+$, 51240-23-4; Co(*N-meso*-$Me_6[14]dieneN_4)(C_2H_3)(H_2O)^{2+}$, 51240-24-5; Co(*N-d,l*-$Me_6[14]dieneN_4)(CH_3)(H_2O)^{2+}$, 47247-33-6; Co(*N-d,l*-$Me_6[14]dieneN_4)(CH_3)(NCS)^+$, 51240-25-6; Co(*N-d,l*-$Me_6[14]dieneN_4)(CH_3)(CN)^+$, 51240-26-7; $Co(Me_6[14]dieneN_4)(NCS)_2{}^+$, 47512-96-9; $Co(Me_6[14]dieneN_4)(CN)_2{}^+$, 17747-64-7; $Co(Me_4[14]tetraeneN_4)(CH_3)(H_2O)^{2+}$, 50600-07-2; $Co(Me_4[14]tetraeneN_4)(CH_3)(NCS)^+$, 51240-27-8; $Co(Me_4[14]tetraeneN_4)(H_2O)_2{}^{3+}$, 36452-48-9; $Co(Me_4[14]tetraeneN_4)(NCS)_2{}^+$, 51240-28-9; $[Co(Me_6[14]dieneN_4)(OH_2)C_2H_3]Cl_2$, 51240-29-0; $[Co(Me_6[14]dieneN_4)(CN)C_2H_3]ClO_4$, 51240-31-4; $[Co(Me_6[14]dieneN_4)(CN)C_2H_3]CN$, 51240-32-5; $[Co(Me_6[14]dieneN_4)(CN)_2]ClO_4$, 16247-32-8; $[Co(Me_6[14]aneN_4)(CN)(CH_3)]ClO_4$, 51240-34-7; $[Co(Me_6[14]aneN_4)(CN)_2]ClO_4$, 51268-46-3.

Contribution No. 3246 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Preparation of η-Cyclopentadienylcobalt(III) and η-Cyclopentadienylnickel(IV) Complexes of the η-7-$B_{10}CH_{11}{}^{3-}$ Carbollide Ligand

RICHARD R. RIETZ, DONALD F. DUSTIN, and M. FREDERICK HAWTHORNE*

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Abstraction of bridging protons from $B_{10}CH_{13}{}^-$ with ethanolic KOH followed by addition of C_5H_6 and anhydrous $CoCl_2$ and subsequent oxidation produces a high yield of the $[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]^-$ ion. Abstraction of $N(CH_3)_3$ and bridging protons from $B_{10}H_{12}C[N(CH_3)_3]$ with sodium in THF followed by the addition of NaC_5H_5 and $NiBr_2 \cdot 2C_2H_4(OCH_3)_2$ and subsequent oxidation gives a low yield of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$. Both metallocarboranes are isoelectronic and isostructural with the icosahedral two-carbon species $(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_9C_2H_{11})$ and contain the metal atom bonded to a B_4C face. At 450° under high vacuum $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$ rearranges to a mixture of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}2\text{-}B_{10}CH_{11})$ and $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}1\text{-}B_{10}CH_{11})$.

Introduction

We have recently reported[1] that cyclopentadienylcobalt complexes of the $B_7CH_8{}^{3-}$ ion are formed in the base degradation of orange $(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}6,7\text{-}B_{10}C_2H_{12})$. Here we describe a direct route to cyclopentadienylcobalt(III) complexes of the known $B_{10}CH_{11}{}^{3-}$ carbollide ion,[2] the first reported member of the $B_nCH_{n+1}{}^{3-}$ series of anions. Anionic bis complexes of $B_{10}CH_{11}{}^{3-}$ with Cr, Mn, Fe, Ni, and Co have already been reported by Knoth, Todd, and coworkers.[2,3]

We have also recently reported[4] a neutral bimetallic species $(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_7CH_8)Ni^{IV}(\eta\text{-}C_5H_5)$ formed by addition of a formal $[Ni^{IV}(\eta\text{-}C_5H_5)]^{3+}$ vertex to the reduced $[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_7CH_8)]^-$ complex. We now report the reconstruction of the icosahedron by the addition of $[Ni^{IV}(\eta\text{-}C_5H_5)]^{3+}$ and $[Co^{III}(\eta\text{-}C_5H_5)]^{2+}$ vertices to the $B_{10}CH_{11}{}^{3-}$ ion. $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$ is the first known member of the $(\eta\text{-}C_5H_5)Ni^{IV}(B_nCH_{n+1})$ series of *neutral* monocarbon metalloboranes.

Results and Discussion

$[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]^-$. The use of cyclopentadienylcobalt carborane complexes has greatly simplified structural interpretations of spectra in the study of the reactions of metallocarborane cages.[5] Recently, an improved synthesis of icosahedral metallocarboranes such as $(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_9C_2H_{11})$ incorporating η-cyclopentadienyl ligands has been developed in this laboratory.[6] This improved method involves the simultaneous abstraction of protons from the $B_9C_2H_{12}{}^-$ ion and from cyclopentadiene by ethanolic potassium hydroxide in the presence of the metal salt. The same synthetic route (eq 1) was followed for the $B_{10}CH_{13}{}^-$ ion and the η-

$$3CoCl_2 + 2C_5H_6 + 2B_{10}CH_{13}{}^- + 6C_2H_5O^- \xrightarrow[C_2H_5OH]{KOH} 2[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_{10}CH_{11})]^- + 6C_2H_5OH + Co^0 + 6Cl^- \quad (1)$$

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(1) (a) D. F. Dustin and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1329 (1972); (b) *Inorg. Chem.*, 12, 1380 (1973).

(2) (a) D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.*, 6, 2229 (1967); (b) W. H. Knoth, *ibid.*, 10, 598 (1971); (c) W. H. Knoth, J. L. Little, and L. J. Todd, *Inorg. Syn.*, 11, 41 (1968).

(3) (a) W. H. Knoth, *J. Amer. Chem. Soc.*, 89, 3342 (1967); (b) D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *ibid.*, 89, 3342 (1967).

(4) C. G. Salentine and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 560 (1973).

(5) (a) M. F. Hawthorne and G. B. Dunks, *Science*, 178, 462 (1972); (b) G. B. Dunks and M. F. Hawthorne, *Accounts Chem. Res.*, 6, 124 (1973).

(6) C. J. Jones and M. F. Hawthorne, *Inorg. Chem.*, 12, 608 (1973).

cyclopentadienylcobalt complex of the carbollide ion was obtained in 85% yield. The collected analytical and physical data obtained for $[(CH_3)_4N]^+[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]^-$ (I) are given in Tables I and II.

The 60-MHz ^1H nmr spectrum (Table III) of $[(CH_3)_4N][(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]$ consisted of two sharp singlets of area ratio 5:12 and a broad singlet of area 1. These signals were assigned to the cyclopentadienyl protons, the tetramethylammonium ion protons, and the single carborane C-H unit, respectively. The 80.5-MHz ^{11}B nmr spectrum (Table IV) consisted of five doublets of area ratios 3:2:1:2:2. The doublet of area 3 was presumably due to the coincidental overlap of an area 2 doublet and an area 1 doublet.

The nmr data are consistent with the proposed structure of the $[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]^-$ ion (Figure 1). The inclusion of a transition metal into the $B_{10}CH_{11}{}^{3-}$ icosahedral fragment has regenerated the icosahedron as was the case for the transition metal complexes of the $B_9C_2H_{11}{}^{2-}$ dicarbollide ion. A qualitatively similar ^{11}B nmr spectrum would be expected for the isomeric $[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}2\text{-}B_{10}CH_{11})]^-$ ion, but the carbon atom probably remains as part of the open, five-membered face adjacent to the cobalt atom.

In keeping with the convention that a metallocarborane may be thought of as a nido carborane ligand η-bonded to the metal, the cyclopentadienyl cobalt complex of the carbollide ion, shown in Figure 1, is correctly named η-cyclopentadienyl-η-undecahydro-7-carba-*nido*-undecaboratocobaltate(1−).[7]

Chemically, the complex was very inert. It was stable in ethanolic potassium hydroxide solution at 100° for 90 hr. Nucleophilic attack by ethoxide ion is unfavorable on electrostatic grounds and the metallocarborane polyhedral contraction process[8] did not occur. The electrochemical oxidation of the cobalt(III) complex was irreversible (Table II) and treatment with $KMnO_4$, $FeCl_3$, or Ce^{4+} salts produced no neutral, cobalt(IV) species. Polyhedral expansion reactions[9] characteristic of neutral $2n + 14$ metallocarboranes and neutral $B_nC_2H_{n+2}$ carboranes could not be effected using the anionic complex, even though bimetallic cyclopentadienyl-cobalt-nickel complexes of $B_nCH_{n+1}{}^{5-}$ ions are known.[4]

$(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$. Insertion of a $[(\eta\text{-}C_5H_5)\text{-}Ni^{IV}]^{3+}$ vertex into the $\eta\text{-}7\text{-}B_{10}CH_{11}{}^{3-}$ ion formed a neutral molecule of icosahedral geometry. η-Cyclopentadienyl-η-undecahydro-7-carba-*nido*-undecaboratonickel(IV), $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$ (II), fulfills the $2n + 14$ electron rule[10] ($n = 12$) with no molecular charge.[11] Of greatest interest must be the predicted chemical similarity[10] of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}B_nCH_{n+1})$ polyhedral frameworks which should exhibit as great a scope of reactions as the analogous dicarbon-cobalt(III)-metallocarborane series.[5,8,9]

Low yields (~5-9%) of II were obtained in tetrahydrofuran (THF) solution using the easily prepared $B_{10}H_{12}CN(CH_3)_3$ species[2] (eq 2-4). Substitution of $(\eta\text{-}C_5H_5)Ni^{II}(CO)I$,[12] or nickelocene, as the $[(\eta\text{-}C_5H_5)Ni^{II}]^+$ source resulted in lower yields (1-5%) of II.

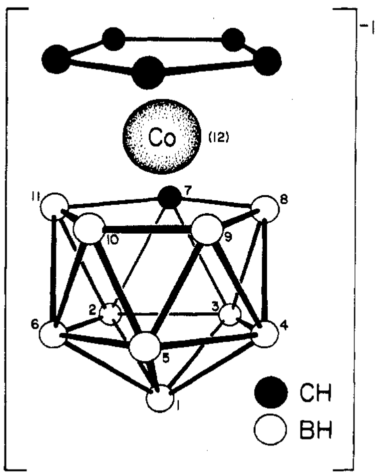

Figure 1. Proposed structure for the $[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]^-$ ion.

$$B_{10}H_{12}CN(CH_3)_3 \xrightarrow[\text{Na, THF, reflux}]{-H_2,\ -N(CH_3)_3} B_{10}CH_{11}{}^{3-} \tag{2}$$

$$B_{10}CH_{11}{}^{3-} \xrightarrow[\text{THF}]{Na^+C_5H_5^-} \xrightarrow[0°]{NiBr_2\cdot 2C_2H_4(OCH_3)_2} (\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}7\text{-}B_{10}CH_{11})^{2-} \tag{3}$$

$$(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}7\text{-}B_{10}CH_{11})^{2-} \xrightarrow[\text{THF}]{O_2} (\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11}) \tag{4}$$

A novel preparation of II involves the "triple-decker sandwich" compound $[(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}C_5H_5)]^+BF_4^-$ recently synthesized by Werner and Salzer.[13] They have reported that this complex is split by strong Lewis bases to form nickelocene and $(\eta\text{-}C_5H_5)NiL_2$ complexes, *e.g.*[14]

$$[(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}C_5H_5)]^+BF_4^- + 2P(C_6H_5)_3 \xrightarrow{(C_2H_5)_2O} (\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}C_5H_5) + \{(\eta\text{-}C_5H_5)Ni^{II}[P(C_6H_5)_3]_2\}^+BF_4^- \tag{5}$$ [14]

Their work suggests that an inner Ni–$(\eta\text{-}C_5H_5)$ bond of the "triple-decker sandwich" compound is cleaved and a $[Ni^{II}\text{-}(\eta\text{-}C_5H_5)]^+$ species is freed to be complexed by the Lewis base. We have found that a slurry of the "triple-decker sandwich" compound in the weak Lewis base THF reacts readily with $B_{10}CH_{11}{}^{3-}$ (prepared as in eq 2), presumably through this same cleavage mechanism, to produce a moderate yield of II (eq 6-9).

$$[(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}C_5H_5)]^+BF_4^- \xrightarrow{\text{THF}} (\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}C_5H_5) + \{[Ni^{II}(\eta\text{-}C_5H_5)]^+\} \tag{6}$$

$$\{[Ni^{II}(\eta\text{-}C_5H_5)]^+\} + B_{10}CH_{11}{}^{3-} \xrightarrow{\text{THF}} [(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}7\text{-}B_{10}CH_{11})]^{2-} \tag{7}$$

$$[(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}7\text{-}B_{10}CH_{11})]^{2-} \xrightarrow[\text{THF}]{O_2} (\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11}) \tag{8}$$

The 80.5-MHz ^{11}B nmr spectrum of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$, Table IV, is in complete accord with the predicted structure (Figure 2A). The 1:2:2:1:2:2 pattern of doublets

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[7] Our approach in this paper is specified under IUPAC rule 7.2, *Pure Appl. Chem.*, 30, 683 (1972); *i.e.*, the ligand is numbered in ascending planes from the vertex opposite the open face with the heteroatom (carbon) receiving the lowest possible number (here, 7).

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[10] C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 543 (1973).

[11] The required 38 electrons are donated by the $\eta\text{-}B_{10}CH_{11}$ ligand (10 × 2 + 1 × 3 = 23), nickel(10), and cyclopentadiene(5).

[12] E. O. Fischer and C. Palm, *Chem. Rev.*, **91**, 1725 (1958).

[13] (a) A. Salzer and H. Werner, *Angew. Chem., Int. Ed. Engl.*, **11**, 930 (1972); (b) H. Werner and A. Salzer, *Syn. Inorg. Metal. Chem.*, **2**, 239 (1972).

[14] A. Salzer and H. Werner, *Syn. Inorg. Metal. Chem.*, **2**, 249 (1972).

Table I. Infrared Spectra and Melting Point Data for $B_{10}CH_{11}{}^{3-}$ Derivatives

No.	Compd	Mp,[a] °C	Infrared spectrum,[b] cm^{-1}
I	$[(CH_3)_4N]^+[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]^-$	>300	3085 m, 2495 s, 1465 s, 1415 s, 1290 w, 1175 w, 1110 s, 1045 s, 1010 s, 972 w, 950 s, 906 m, 893 w, 858 s, 828 s, 734 w, 711 m
II	$12\text{-}(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$	310[c]	3060 w, 2560 s, 1410 s, 1340 m, 1268 w, b, 1160 vw, sh, 1130 m, 1100 w, 1080 vw, 1035 m, 1020 m, 995 s, 950 m, 930 w, 890 w, 870 vw, 840 s, 826 m, sh, 775 w, 696 vw
III	$12\text{-}(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}2\text{-}B_{10}CH_{11})$	233.5[c]	3060 w, 2530 s, 1420 s, 1165 vw, 1120 vw, 1055 m, 1020 w, 998 s, 955 vw, 920 m, 898 w, 880 vw, 840 s, 735 m, 690 w
IV	$12\text{-}(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}1\text{-}B_{10}CH_{11})$	217.5[c]	3065 w, 2530 s, 1415 s, 1140 vw, 1065 s, 1015 m, 975 w, 945 s, 928 m, sh, 912 w, sh, 875 w, 842 s, 741 w

[a] Sealed capillary. [b] Nujol mull. [c] ±0.5°.

Table II. Analytical Data, $E_{p/2}$ Values, and Electronic Spectra of $B_{10}CH_{11}{}^{3-}$ Derivatives

	Elemental analyses, %											
Compd	C		H		B		Co or Ni		N			
no.	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	$E_{p/2}$, V *vs.* sce	Electronic spectra,[a] λ_{max}, mμ (ε)
I	36.47	36.28	8.51	8.59	32.83	32.02	17.93	17.61	4.26	4.29	+1.07[b,c]	416 (296), 303 sh (1900), 267 (39,700), 232 sh (6320)
II	28.24	28.27	6.33	6.43	42.40	42.27	23.03	23.28			−0.27[d,f] −1.57[e,f] −2.43[c,f]	358 sh (1780), 278 (31,300), 231 sh (2800)
III	28.24	28.41	6.33	6.60	42.40	42.37	23.03	22.96			−1.52[d,g] −2.65[c,e,g]	342 (1370), 271 (37,000), 236 sh (6700)
IV	28.24	28.46	6.33	6.51	42.40	42.27	23.03	22.95			−0.92[d,g] −2.05[c,e,g]	349 (133), 280 (33,500), 227 sh (5760)

[a] In Spectroquality acetonitrile. [b] $Co^{III} - e^- \rightarrow Co^{IV}$ determined in acetonitrile with 0.1 *F* tetraethylammonium perchlorate as supporting electrolyte; platinum button electrode. [c] Irreversible. [d] $Ni^{IV} + e^- \rightarrow Ni^{III}$. [e] $Ni^{III} + e^- \rightarrow Ni^{II}$. [f] Determined in acetonitrile with 0.1 *F* tetraethylammonium perchlorate as supporting electrolyte; hanging mercury drop electrode. [g] Determined in methylene chloride with 0.1 *F* tetrabutylammonium perchlorate as supporting electrolyte; platinum button electrode.

Table III. ^1H Nmr Data for $B_{10}CH_{11}{}^{3-}$ Derivatives[a]

Compd no.	Carborane C-H	$\eta\text{-}C_5H_5$	$(CH_3)_4N$ protons
I[b]	7.36 (1)	4.92 (5)	6.89 (12)
II[c]	5.68 (1)	3.57 (5)	
III[c]	6.83 (1)	3.88 (5)	
IV[c]	5.75 (1)	4.16 (5)	

[a] τ, relative to TMS = 10.0 (relative intensity). [b] CD_3CN solution. [c] $(CD_3)_2CO$ solution.

Table IV. 80.5-MHz ^{11}B Nmr Spectra of $B_{10}CH_{11}{}^{3-}$ Derivatives

Compd	Rel intens	Chem shifts, δ[a] (J_{BH}, Hz)
I[b]	3:2:1:2:2	−0.6 (125), +5.5 (147), +9.4 (128), +13.9 (131), +19.4 (141)
II[c]	1:2:2:1:2:2	−21.7 (~110), −20.0 (~140), −10.0 (161), −0.6 (~110), +0.9 (~125), +9.5 (158)
III[d]	1:1:2:2:4	−20.0 (158), −14.0 (~145), −12.7 (~130), −6.4 (169), +6.9 (~150)
IV[d]	1:1	−10.0 (148), +12.5 (159)

[a] Relative to $BF_3 \cdot O(C_2H_5)_2 = 0$. [b] CH_3CN solution. [c] Acetone-d_6 solution. [d] CH_2Cl_2 solution.

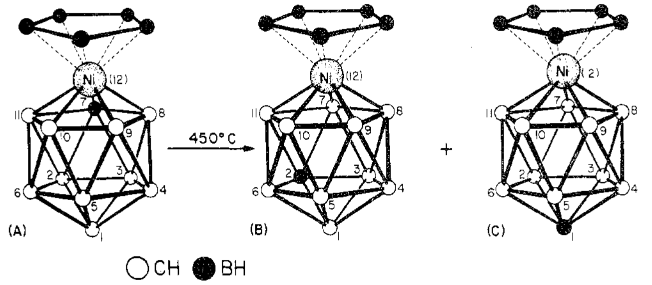

Figure 2. Proposed structures and numbering for $(\eta\text{-}C_5H_5)Ni^{II}(\eta\text{-}B_{10}CH_{11})$ isomers. See text for discussion of nomenclature.

is the predicted pattern for the $(\eta\text{-}7\text{-}B_{10}CH_{11})^{3-}$ ligand. The 60-MHz ^1H nmr spectrum, Table III, displays the expected cyclopentadienyl and carborane C-H resonances in relative intensities 5:1.

The mass spectrum at 70 eV exhibits a peak at *m/e* 262 (calcd for $^{64}Ni^{11}B_{10}{}^{12}C_6{}^1H_{16}{}^+$, 262.1462; found, 262.1463). At 12 eV the molecular envelope is centered about *m/e* 255 and the relative intensities of the peaks correspond within 10% of those from a computer simulation[15] of the statistical distribution of molecular ions for $NiB_{10}C_6H_{16}$.

$(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}2\text{-}B_{10}CH_{11})$ and $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}1\text{-}B_{10}CH_{11})$. The predicted isomerization[10] of $(\eta\text{-}C_5H_5)Ni^{IV}\text{-}(\eta\text{-}7\text{-}B_{10}CH_{11})$ occurs above 350° (see Table V). The rearrangement parallels that of $1,2\text{-}B_{10}C_2H_{12}$ in that the heteroatom positional isomers formed (compounds III and IV) may be viewed as being similar to 1,7- and $1,12\text{-}B_{10}C_2H_{12}$. This isomerization reaction bears a close resemblance to that of $(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7,8\text{-}B_9C_2H_{11})$ since more than one isomer is present at any given temperature.[16]

The proposed structure of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}2\text{-}B_{10}CH_{11})$ (III), Figure 2B, would imply a 2:2:1:2:2:1 pattern in the ^{11}B nmr spectrum. The observed 1:1:2:2:4 pattern, Table IV, at 80.5 MHz, undoubtedly contains one area 4 doublet arising from the accidental overlap of two doublets of intensity 2. The 60-MHz ^1H nmr spectrum (Table III) exhibited the expected cyclopentadienyl and carborane C-H resonances in

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(15) ISOTOPE, a program written by E. Hoel, Department of Chemistry, University of California at Los Angeles.

(16) (a) M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 93, 4912 (1971); (b) *ibid.*, 94, 6679 (1972).

Table V. Rearrangement Data for 12-(η-C_5H_5)Ni(η-7-$B_{10}CH_{11}$)

	%			
Temp, °C	Recovered 12,7 isomer	12,2 isomer	12,1 isomer	Total
350	71	3	2	76
400	14	42	31	87
450	2	50	32	84
500		44	19	63
550		33	9	42
600		13	2	15

a 5:1 ratio. The mass spectrum at 70 eV displayed a strong molecular envelope ending at *m/e* 260 with a most intense peak at *m/e* 254. At 12 eV the observed parent envelope is centered about *m/e* 255 and matches the theoretical distribution of peaks[15] within 5%. Additional data are found in Tables I and II.

The 80.5-MHz ^{11}B nmr spectrum (Table IV) of (η-C_5H_5)-Ni^{IV}(η-1-$B_{10}CH_{11}$) (IV) displayed the two doublets of equal intensity that would be expected for the two distinct, five-membered boron belts in the predicted structure (see Figure 2C). Again, the 60-MHz ^1H nmr spectrum (Table III) displayed the characteristic cyclopentadienyl and carborane C-H resonances in relative areas 5:1. The mass spectrum at 70 eV displayed a strong molecular envelope centered at *m/e* 254 and ending at *m/e* 260. At 12 eV the parent envelope had a base peak at *m/e* 255 and closely resembled (±5%) the calculated envelope for a $NiB_{10}C_6H_{16}$ species.[15] Additional data are presented in Tables I and II.

The structure of the 1,12 isomer suggests that no boron atoms should possess a center of positive charge and be subject to nucleophilic attack. Accordingly, a 94% recovery of the 1,12 nickel(IV) complex was realized after refluxing in ethanolic potassium hydroxide for 2 days.

Experimental Section

Physical Measurements. Proton nmr spectra were obtained with a Varian A-60D spectrometer. The 80.5-MHz ^{11}B nmr spectra were obtained by the Fourier transform technique on an instrument designed and constructed by Professor F. A. L. Anet of this department. Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Ultraviolet-visible spectra were measured on a Cary 14 spectrophotometer. Cyclic voltammetry was performed on an instrument based on the design of Lawless and Hawley.[17] Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Mass spectra were obtained with an Associated Electrical Industries Model MS-9 spectrometer with exact mass measurements being made relative to known peaks of perfluorotributylamine.

Materials. Anhydrous $CoCl_2$ was prepared by heating $CoCl_2 \cdot 6H_2O$ (Matheson Coleman and Bell) at 100° under high vacuum for 3 days. The $NiBr_2 \cdot 2C_2H_4(OCH_3)_2$ was prepared by the method of King[18] using 325 mesh nickel powder (ROC/RIC). *Warning*! $NiBr_2 \cdot 2C_2H_4(OCH_3)_2$ *has been found to cause contact dermatitis upon contact with skin and should be handled appropriately*. Nickelocene was prepared by the method of Jolly.[19] $[(\eta\text{-}C_5H_5)_3Ni_2]^+BF_4^-$ was prepared by the HBF_4 route of Salzer and Werner.[13a] The (η-C_5H_5)Ni(CO)I was prepared from $[(\eta\text{-}C_5H_5)NiCO]_2$ (Ventron) and iodine in *n*-hexane.[12] Dicyclopentadiene (Aldrich) was converted to C_5H_6 immediately prior to use. Tetrahydrofuran was freshly distilled from $LiAlH_4$ and collected under N_2. THF solutions of NaC_5H_5 were prepared as previously described.[20] 1,2-Dimethoxyethane (monoglyme) was refluxed over sodium for 2 days and then distilled twice from fresh sodium under N_2. Preparations of $B_9CH_{10}^-$, $B_9H_{11}N(CH_3)_3$, $B_{10}CH_{13}^-$, $B_{10}H_{12}CN(CH_3)_3$, and $B_{11}CH_{12}^-$ have been detailed by Knoth, Todd, and coworkers.[2,3]

$[(CH_3)_4N][(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]$ (I). A 10-g (150 mmol of 85% pellets) quantity of potassium hydroxide was dissolved in 100 ml of degassed absolute ethanol in a 500-ml, three-necked, round-bottom flask. The flask was fitted with a mechanical stirrer and a reflux condenser topped with a nitrogen inlet. The solution was cooled to approximately 15° with an ice bath, and 5 g (75 mmol) of freshly distilled cyclopentadiene, dissolved in ethanol, was added dropwise from an addition funnel. A 4-g (30-mmol) amount of anhydrous $CoCl_2$ was added from an addition funnel as a slurry in 50 ml of ethanol. The reaction mixture was stirred for 1 hr at room temperature.

A 2.66-g (10-mmol) sample of $CsB_{10}CH_{13}$ dissolved in 50 ml of ethanol was then added and the mixture was stirred at room temperature for 17 hr during which time the color changed from bluish gray to yellow-brown. A 5-g (75-mmol) amount of additional potassium hydroxide was added and the reaction mixture was stirred for 2 hr at room temperature and then 5 hr at the reflux temperature. The mixture had then assumed a green color.

After cooling to room temperature, the reaction mixture was poured into 500 ml of water, stirred well, and then filtered through a medium-porosity frit. To the filtrate was added 20 g of tetramethylammonium chloride dissolved in 50 ml of water. The resulting yellow precipitate was filtered, washed with water, and redissolved in 20% acetonitrile–dichloromethane. The solution was dried with $MgSO_4$ and filtered. The addition of hexane to the filtrate followed by slow rotary evaporation of the solvent produced 2.8 g (8.5 mmol, 85%) of bright yellow crystals of $[(CH_3)_4N][(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]$.

(η-C_5H_5)Ni^{IV}(η-7-$B_{10}H_{11}$) (II). In a 1-l. three-necked flask fitted with a mechanical stirrer equipped with a glass paddle, a coil condenser, a nitrogen inlet, an addition funnel, and an outlet at the bottom containing a course glass frit and closed with a Teflon stopcock was placed 3 g of Na dispersion (50% in oil, 65 g-atoms). The Na was washed free of the oil and preservative using four 30-ml portions of THF. Fresh THF (200 ml) was added to the flask. A slurry of 3.2 g of $B_{10}H_{12}CN(CH_3)_3$ (16.0 mmol) in 50 ml of THF was slowly added through the addition funnel. When the initial H_2 evolution ceased, the addition funnel was removed. A heating tape was wrapped about the flask and the mixture was refluxed under N_2 for 18 hr.

The flask was cooled, the heating tape removed, and the flask cooled to 0°. A separately prepared solution of 174 mmol of NaC_5H_5 [20] in 100 ml of THF was filtered into the reaction flask.

Pulverized $NiBr_2 \cdot 2C_2H_4(OCH_3)_2$ (8 g, 20 mmol) was loaded into an addition funnel in a N_2 drybox. This was added as a slurry in 50 ml of THF to the vigorously stirred reaction pot over a 10-min period. The reaction mixture immediately turned green-black. The flask was stirred at 0° for 2 hr after which it was allowed to warm slowly to room temperature (~10 hr). At this time, the flask was opened to the air and oxygen was bubbled in through a fritted inlet (2 hr).

The brown slurry was filtered through Celite. Approximately 15 g of an intractable, gummy green residue remained on the Celite. Oxygen was bubbled through the green-black filtrate for 2 hr. The filtrate was then filtered through a medium frit and stripped onto 10 g of silica gel. This was mounted on a 1.5 in. × 15 in. silica gel column and eluted with hexane–methylene chloride. Very faint yellow and purple bands eluted first followed by an intense orange band. Preliminary ^{11}B nmr and mass spectra have suggested the yellow compound is 1,10-(η-C_5H_5)Ni(η-1-B_8CH_9). This material is currently under investigation.[21] The purple compound was identified as (η-C_5H_5)Ni[η-7-$B_{10}H_{10}CNH(CH_3)_2$].[22] The orange band was stripped to dryness and recrystallized from hexane–CH_2Cl_2 to give 0.353 g of orange platelets. The yield of (η-C_5H_5)Ni(η-7-$B_{10}CH_{11}$) was 8.6%.

The column was washed with CH_3CN. The red eluate was stripped to dryness (~2 g), dissolved in water, filtered, and treated with $(C_2H_5)_4NBr$. Boron-11 spectra of the precipitate in CH_3CN showed this to be an approximately 1:1 mixture of the $B_9CH_{10}^-$ and $[Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})_2]^{2-}$ ions.

Reaction of $(\eta\text{-}7\text{-}B_{10}CH_{11})^{3-}$ and $[(\eta\text{-}C_5H_5)_3Ni_2]^+BF_4^-$. A slurry of 0.45 g of $Na_3B_{10}CH_{11} \cdot THF$ (1.5 mmol) in 100 ml of THF was prepared as previously described[2] and placed into a 250-ml three-necked flask under N_2. In a drybox, 0.6 g of $[(\eta\text{-}C_5H_5)_3Ni_2]^+BF_4^-$

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(1.50 mmol) was loaded into an addition funnel. The funnel was placed on the reaction flask and the nickel complex was quickly washed into the rapidly stirred slurry with 10 ml of THF. A deep red-orange solution formed. The mixture was stirred at room temperature for 1 hr. The flask was opened to the air and stirring was continued for 12 hr. The solution was filtered and stripped onto ~1 g of silica gel. This was mounted on a 1.25 in. × 8 in. column and eluted with hexane–CH_2Cl_2. The one orange band that eluted was identified by ^1H and ^{11}B nmr spectra as 0.068 g of pure II (0.27 mmol, 18%). Washing the column with CH_3CN gave 0.319 g of a red compound identified as $[(\eta\text{-}C_5H_5)_2Ni]^+B_9CH_{10}^-$.

Isomerization of $(\eta\text{-}C_5H_5)Ni(\eta\text{-}7\text{-}B_{10}CH_{11})$. In a typical rearrangement, 0.177 g of $(\eta\text{-}C_5H_5)Ni(\eta\text{-}7\text{-}B_{10}CH_{11})$ (II) (0.693 mmol) was weighed into a 10-ml Pyrex flask. This was fitted to a 12 mm × 500 mm Vycor tube attached to a vacuum line. A 200-mm segment of the lower portion of this tube was wrapped with asbestos insulation and nichrome heating wire. The system was evacuated (10^{-5} mm) and the heated section was raised to 450° (monitored by a chromel-alumel thermocouple). The Pyrex bulb was slowly heated to ~200° with an air heat gun to sublime II slowly into the hot zone. The volatile products collected on the cool unwrapped upper portion of the Vycor tube. After cooling, the system was filled with N_2 and opened; the products were washed out with CH_2Cl_2. Filtration collected some black metallic flakes (Ni metal). The orange filtrate was stripped unto 1 g of silica gel and eluted on a 1 in. × 12 in. silica gel column using hexane–CH_2Cl_2.

Three products eluted. The first band (R_f 73, R_f(hexane) 100) was recrystallized from hexane–CH_2Cl_2 to give 0.057 g (0.223 mmol, 32%) of long yellow needles of $(\eta\text{-}C_5H_5)Ni(\eta\text{-}1\text{-}B_{10}CH_{11})$ (IV). The second band (R_f 54) was recrystallized from hexane-CH_2Cl_2 to give 0.089 g (0.349 mmol, 50%) of yellow-orange plates of $(\eta\text{-}C_5H_5)Ni(\eta\text{-}2\text{-}B_{10}CH_{11})$ (III). The third band (R_f 23) yielded 0.004 g (0.015 mmol, 2%) of orange crystals identified as unchanged II. Total recovery was 84%. Other runs are given in Table V.

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Registry No. I, 51329-55-6; II, 51329-56-7; III, 51329-57-8; IV, 51329-58-9; $[(\eta\text{-}C_5H_5)_2Ni]^+B_9CH_{10}^-$, 51518-87-7; $CsB_{10}CH_{13}$, 51391-30-1; $B_{10}H_{12}CN(CH_3)_3$, 31117-16-5; $NiBr_2\cdot 2C_2H_4(OCH_3)_2$, 18346-62-8; $Na_3B_{10}CH_{11}$, 51391-29-8; $[(\eta\text{-}C_5H_5)_3Ni_2]^+BF_4^-$, 37298-59-2.

Contribution from the Department of Chemistry,
Rochester Institute of Technology, Rochester, New York 14623

Steric Constraints in Coordination Reactions. Kinetic Study of the Reaction of Aquonickel(II) with *N*-Methyl-Substituted Ethylenediamines

THOMAS S. TURAN

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The formation and dissociation rates of the 1:1 complexation reactions of aquonickel(II) ion with *N,N*-dimethylethylenediamine, *N,N'*-dimethylethylenediamine, and *N,N,N'*-trimethylethylenediamine have been investigated at 25.0° and 0.1 *M* ionic strength over a pH range of 5.7–7.6 using stopped-flow kinetic techniques. Protonation constants of the ligands and the 1:1 stability constants of the Ni(II) complexes were also determined. Formation reactions in all cases were first order in Ni(II) and in ligand. Steric effects superimposed upon internal conjugate base rate enhancements are seen for the reactions with unprotonated ligands. Evidence for the presence of steric constraints in dissociation rate steps is also presented. Tentative estimates of the magnitude of internal conjugate base effects are made and presented in graphical form.

Introduction

The general features of the octahedral complexation reactions of aquometal ions with a wide variety of ligands have been thoroughly studied[1–3] and are well known. In particular, hexaaquonickel(II) has been the subject of intensive study in recent years.[4,5] It has become apparent and is generally accepted that a dissociative mechanism, as proposed by Eigen,[6] involving a rapid diffusion-controlled association of reactants to form an "outer-sphere" complex followed by the rate-determining step of metal–water bond rupture, is the mechanistic pathway for reactions of nickel(II) with most ligands. However, recent studies of the reactions of Ni(II) ion with alkylamines[7] and *N*-alkyl-substituted ethylenediamines[8] have shown that steric constraints exert a pronounced rate-depression effect on the formation rate constants.

Other ligands such as *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine (TKED) and *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine (THPED)[9,10] and β-alanine[11] react anomalously slowly with Ni(II) and Co(II). These results have been rationalized by assuming that the rate-determining step in the reaction mechanism is shifted to the loss of a second water molecule. In these reactions, "sterically controlled substitution" may occur when steric constraints block "normal substitution"[4] or when chelate ring closure is sufficiently slow so as to become the rate-determining step. In studies with highly basic N-substituted diamines,[8,9] an internal conjugate base (ICB) mechanism has been postulated[12] to explain anomalously rapid reaction rates which are ap-

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