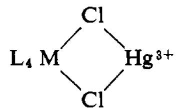
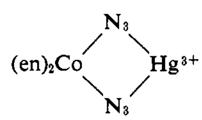


(where L_4 M = $(en)_2Co$, $(H_2O)_4Cr)^{2,6}$ or[38]



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(37) T. R. Musgrave and R. N. Keller, *Inorg. Chem.*, 4, 1793 (1965).

is necessary before sufficient stability is conferred for direct detection.[39]

(38) D. A. Loeliger and H. Taube, *ibid.*, 5, 1376 (1966).

(39) Note Added in Proof. After this paper was submitted, a measurement of the equilibrium quotient for reaction 7 of Table III was published: L. Ciavatta and M. Grimaldi, *Inorg. Chim. Acta*, 4, 312 (1970). These authors report a value of 1.2×10^9 at 25° and ionic strength 1.0 (sodium perchlorate), to be compared with our estimated value of $\sim 2 \times 10^9$. With the more accurate value for Q_7, the following quantities can be calculated: Q and k_r for reaction 2, 5.1×10^2 and 17×10^{-8}; Q and k_r for reaction 3, 8.5×10^6 and 17×10^{-8}; Q and k_r for reaction 4, 2.4×10^{12} and 0.013×10^{-8}.

Chelated Biscarborane Transition Metal Derivatives Formed through Carbon–Metal σ Bonds

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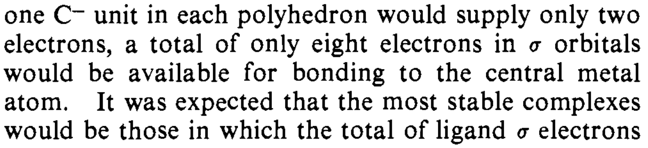
Abstract: Biscarborane $[1\text{-}(1'\text{-}1',2'\text{-}B_{10}C_2H_{11})\text{-}1,2\text{-}B_{10}C_2H_{11}]$ reacts with 2 mol equiv of *n*-butyllithium in ethyl ether to form 2,2′-dilithiobiscarborane. Dilithiobiscarborane (2 mol equiv) reacts with transition metal halides to form a series of unusually stable anionic chelated transition metal biscarborane derivatives containing metal–carbon σ bonds. The preparation, characterization, reactions, and proposed structures and bonding of these complexes are discussed.

Numerous π-bonded transition metal complexes with $B_9C_2H_{11}^{2-}$, $B_7C_2H_9^{2-}$, and $B_6C_2H_8^{2-}$ ligands have been prepared in this laboratory.[1-9] In addition, several examples of σ-bonded transition metal complexes involving single carbon–metal bonds with $1,2\text{-}B_{10}C_2H_{11}^-$, $1,7\text{-}B_{10}C_2H_{11}^-$, and $1,10\text{-}B_8C_2H_9^-$ and their C-monosubstituted derivatives have been reported.[10,11] In addition, a transition metal complex of the bidentate σ-bonding $1,10\text{-}B_8C_2H_8^{2-}$ ion has been described.[11] One of the bipolyhedral carborane systems, biscarborane $[1\text{-}(1'\text{-}1',2'\text{-}B_{10}C_2H_{11})\text{-}1,2\text{-}B_{10}C_2H_{11}]$[12] (Figure 1), offered the additional opportunity to form the first examples of chelated transition metal carborane complexes through formation of a ring consisting of the metal ion and the four carbon atoms of the two connected polyhedra. The latter study comprises the subject of this paper.

Dupont and Hawthorne[12] reported that biscarborane reacts with 2 mol equiv of *n*-butyllithium in diethyl ether to form *n*-butane and 2,2′-dilithiobiscarborane $[1\text{-}(1'\text{-}2'\text{-}Li\text{-}1',2'\text{-}B_{10}C_2H_{10})\text{-}2\text{-}Li\text{-}1,2\text{-}B_{10}C_2H_{10}]$ as follows



We subsequently observed[13] that the reaction of two of these 2,2′-dilithiobiscarborane units with anhydrous transition metal halides afforded the first examples of ionic σ-bonded[14] transition metal complexes. Since one C^- unit in each polyhedron would supply only two electrons, a total of only eight electrons in σ orbitals would be available for bonding to the central metal atom. It was expected that the most stable complexes would be those in which the total of ligand σ electrons and metal ion d electrons approached 18. Thus, metal ions with d^6, d^7, d^8, d^9, and d^{10} configurations appeared feasible for study. Attempts were made to

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(1) M. F. Hawthorne, *Accounts Chem. Res.*, 1, 281 (1968).

(2) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, 90, 879 (1968).

(3) M. F. Hawthorne and T. A. George, *ibid.*, 89, 7114 (1967).

(4) M. F. Hawthorne and A. D. Pitts, *ibid.*, 89, 7115 (1967).

(5) T. A. George and M. F. Hawthorne, *ibid.*, 90, 1661 (1968).

(6) J. N. Francis and M. F. Hawthorne, *ibid.*, 90, 6553 (1968).

(7) T. A. George and M. F. Hawthorne, *ibid.*, 91, 5475 (1969).

(8) M. F. Hawthorne and H. Ruhle, *Inorg. Chem.*, 8, 176 (1969).

(9) G. B. Dunks and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 92, 7213 (1970).

(10) S. Bresadola, P. Sigo, and A. Turco, *Chem. Commun.*, 1205 (1968).

(11) J. C. Smart, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 91, 1031 (1969).

(12) J. A. Dupont and M. F. Hawthorne, *ibid.*, 86, 1643 (1964).

(13) D. A. Owen and M. F. Hawthorne, *ibid.*, 92, 3194 (1970).

(14) For the sake of brevity and clarity, we have chosen to represent these unusually stable complexes as simple σ-bonded chelates containing M^{n+} ions and 2,2′-biscarboranyl^{2-} ligands. However, ^{11}B nmr, electronic spectra, and electrochemical data strongly indicate that further bonding involving π-type orbitals on both ligand and metal combine to give these complexes their unusual stability not found in other systems containing simple carbon–metal σ bonds. The accessibility of multiple oxidation states for each metal also indicates that electron delocalization in the ligand polyhedra is important in the formation of these complexes.

Table I. Melting Points, Yields, and Analytical Data for the $[(C_2H_5)_4N]_nM^{(4-n)+}[(B_{10}C_2H_{10}-)_2]_2$ Derivatives[a]

			Analyses											
			Calcd, %						Found, %					
Compound	Mp, °C	Yield, %	B	C	H	N	M	Mol wt	B	C	H	N	M	Mol wt
$[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10}-)_2]_2$	210–212	54	56.77	25.21	7.94	1.84	8.43	762.2	56.64	25.49	7.94	1.96	8.57	753[b]
$[(C_2H_5)_4N]_2Cu^{II}[(B_{10}C_2H_{10}-)_2]_2$	221–223	80	48.45	32.27	9.05	3.12	7.11	892.4	45.29	32.14	9.02	3.43	7.85	867[c]
$[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2$	259–262	73	48.84	32.45	9.21	3.15	6.61	888.4	48.41	32.29	9.21	3.45	6.55	912[c]
$[(C_2H_5)_4N]Ni^{III}[(B_{10}C_2H_{10}-)_2]_2$	178–181	76	57.08	25.36	7.97	1.85	7.74	758.2	55.25	25.90	8.24	1.82	7.90	764[c]
$[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$	275–277	75	48.75	32.50	9.19	3.16	6.64	888.7	48.36	32.38	9.32	3.37	6.56	894[c]
$[(C_2H_5)_4N]Co^{III}[(B_{10}C_2H_{10}-)_2]_2$	195–196	83	57.07	25.34	7.96	1.86	7.77	758.5	57.17	25.66	7.93	1.90	8.14	763[c]
$[(C_2H_5)_4N]_2Zn^{II}[(B_{10}C_2H_{10}-)_2]_2$	227–231	85	48.41	32.11	9.02	3.13	7.31	894.1	48.17	32.24	9.08	3.33	7.41	909[c]

[a] M = Cu, Ni, Co, Zn; $n = 1, 2$. [b] Osmometric in ethyl acetate. [c] Osmometric in 2-butanone.

synthesize bis-σ,σ-2,2′-biscarboranyl complexes of representative transition metal ions with these d-electron configurations. It was expected that these complexes would have either pseudotetrahedral, tetragonal, or planar configurations, depending upon the nature of the metal ion involved.[13]

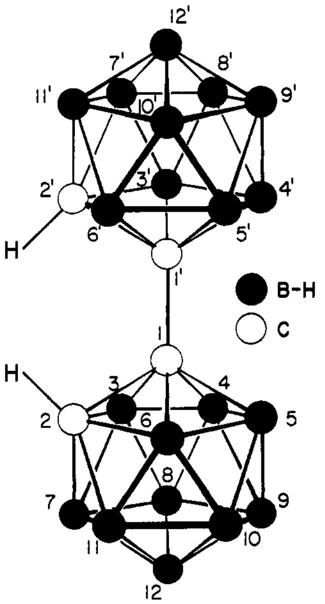

Figure 1. The structure and numbering system for biscarborane [1-(1′-1′,2′-$B_{10}C_2H_{11}$)-1,2-$B_{10}C_2H_{11}$].

Table II. Infrared Spectra of Nujol Mulls of the $[(C_2H_5)_4N]_nM^{(4-n)+}[(B_{10}C_2H_{10}-)_2]_2$ Derivatives[a]

Compound	Absorbance, cm^{-1}
$[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10}-)_2]_2$	2500 (s), 1170 (s), 1072 (s), 1030 (m), 999 (m), 928 (w), 782 (m), 735 (sh), 725 (s)
$[(C_2H_5)_4N]_2Cu^{II}[(B_{10}C_2H_{10}-)_2]_2$	2520 (s), 1185 (s), 1052 (sh), 1030 (m), 1000 (s), 956 (w), 851 (w), 785 (s), 732 (s), 725 (s)
$[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2$	2520 (s), 1300 (w), 1185 (s), 1170 (s), 1070 (s), 1030 (m), 1003 (m), 928 (w), 796 (s), 783 (sh), 733 (s), 724 (sh)
$[(C_2H_5)_4N]Ni^{III}[(B_{10}C_2H_{10}-)_2]_2$	2550 (s), 1300 (w), 1172 (s), 1071 (s), 1059 (sh), 1053 (sh), 1035 (sh), 1001 (m), 928 (w), 781 (m), 735 (sh), 726 (s)
$[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$	2550 (s), 1299 (w), 1186 (s), 1170 (s), 1070 (s), 1051 (w), 1031 (m), 1003 (m), 958 (w), 851 (w), 810 (sh), 793 (sh), 730 (sh), 719 (s)
$[(C_2H_5)_4N]Co^{III}[(B_{10}C_2H_{10}-)_2]_2$	2530 (s), 1400 (sh), 1295 (m), 1180 (s), 1062 (s), 1025 (m), 1005 (sh), 926 (w), 833 (m), 790 (s), 740 (sh), 719 (s)
$[(C_2H_5)_4N]_2Zn^{II}[(B_{10}C_2H_{10}-)_2]_2$	2550 (s), 1299 (w), 1186 (s), 1170 (s), 1070 (s), 1053 (m), 1031 (m), 1003 (m), 958 (w), 929 (w), 851 (w), 810 (sh), 793 (sh), 731 (sh), 720 (s)

[a] M = Cu, Ni, Co, Zn; $n = 1, 2$.

Table III. Electronic Spectra in CH_3CN Solution of the $[(C_2H_5)_4N]_nM^{(4-n)+}[(B_{10}C_2H_{10}-)_2]_2$ Derivatives[a]

Compound	Maxima, mμ (ϵ)
$[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10}-)_2]_2$	374 (28,400), 272 (14,000), 200 (sh, 9000)
$[(C_2H_5)_4N]_2Cu^{II}[(B_{10}C_2H_{10}-)_2]_2$	552 (1030), 334 (13,000), 271 (40,000)
$[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2$	448 (575), 219 (18,200)
$[(C_2H_5)_4N]Ni^{III}[(B_{10}C_2H_{10}-)_2]_2$	375 (4600), 265 (25,200), 223 (24,000)
$[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$	602 (sh, 375), 584 (890), 563 (sh, 650), 254 (14,000), 229 (15,500)
$[(C_2H_5)_4N]Co^{III}[(B_{10}C_2H_{10}-)_2]_2$	548 (sh, 4600), 330 (13,000), 274 (5400), 241 (8200)
$[(C_2H_5)_4N]_2Zn^{II}[(B_{10}C_2H_{10}-)_2]_2$	240 (sh, 1820), 222 (6300)

[a] M = Cu, Ni, Co, Zn; $n = 1, 2$.

Results and Discussion

Preparation and Characterization of the Bis-σ,σ-2,2′-biscarboranyl–Copper Complexes. When a slurry of 2,2′-dilithiobiscarborane was stirred in anhydrous diethyl ether at the reflux temperature for 3 hr with 1 mol equiv of anhydrous cupric chloride, an intensely colored blue solid immediately formed which was rapidly converted to a yellow-brown solid. Cation exchange and isolation as the tetraethylammonium salt afforded 54% of yellow diamagnetic crystalline $[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10}-)_2]_2$, mp 210–212°. Analytical and molecular weight data are presented in Table I. The infrared spectrum (Table II) contained a strong stretching absorption at 2500 cm^{-1}, which indicated B–H groups in an anionic environment.[2,15] The spectrum was marked by the absence of a typically strong and sharp biscarborane C–H stretching absorption at 3040 cm^{-1}.[12] Bands indicative of the tetraethylammonium cation were identified. The electronic spectrum in CH_3CN consisted of three maxima in the visible and ultraviolet regions (Table III). The yellow crystals were stable in air for weeks at a time, but acquired a brownish tinge over a period of months.

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[15] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, 90, 862 (1968).

The 60-MHz ^1H nmr spectrum in deuterioacetone exhibited only the resonances of the $(C_2H_5)_4N$ cation and no resonances attributable to carborane C–H protons. A triplet of triplets at τ 8.60 (J = 7.2, J' = 1.8) of intensity 3 was assigned to the cation methyl protons while the quartet at τ 6.52 (J = 7.2) of intensity 2 was assigned to the cation methylene protons. The 32.1-MHz ^{11}B nmr spectrum consisted of two sets of overlapping doublets at +3.9 and −0.5 ppm relative to $BF_3 \cdot O(C_2H_5)_2$.

From the infrared and ^1H nmr data, which indicated the product to be a diamagnetic anion containing only B–H units and no C–H units from biscarborane, and from the electronic spectrum, which indicated the metal ion to be diamagnetic Cu^{III} (d^8), we proposed[13] that the copper atom in the complex was σ bonded to the four carbon atoms of the four polyhedra of two 2,2′-biscarboranyl units. We propose the structure presented in Figure 2 for $[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10}-)_2]_2$, wherein the copper atom and the eight carbon atoms of the four carborane polyhedra are coplanar. This planar configuration might be the one expected for any diamagnetic d^6 or d^8 ion, or for any low-spin d^7 ion.

The blue complex seen as an apparent intermediate in the preparation of the yellow $Cu^{III}[(B_{10}C_2H_{10}-)_2]_2^-$ was found to be the $Cu^{II}[(B_{10}C_2H_{10}-)_2]_2^{2-}$ ion, which is apparently oxidized to the yellow Cu^{III} derivative by cupric chloride with simultaneous formation of cuprous chloride

$$CuCl_2 + 2Li_2(B_{10}C_2H_{10}-)_2 \xrightarrow[40°]{(C_2H_5)_2O} 2LiCl + Li_2Cu^{II}[(B_{10}C_2H_{10}-)_2]_2$$

$$CuCl_2 + Li_2Cu^{II}[(B_{10}C_2H_{10}-)_2]_2 \longrightarrow LiCl + CuCl + LiCu^{III}[(B_{10}C_2H_{10}-)_2]_2$$

This blue Cu^{II} derivative was subsequently prepared by reduction of the yellow Cu^{III} derivative with lithium metal in acetone solution or with zinc metal in dichloromethane solution in the presence of $(C_2H_5)_4NBr$

$$Cu^{III}[(B_{10}C_2H_{10}-)_2]_2^- + e^- \xrightarrow[Zn,\ CH_2Cl_2]{Li,\ (CH_3)_2CO} Cu^{II}[(B_{10}C_2H_{10}-)_2]_2^{2-}$$

The reduction product was isolated as the tetraethylammonium salt in 55–80% yield, depending upon the method of preparation. The analytical and molecular weight data for the blue paramagnetic needles, mp 221–223° dec, are presented in Table I. Its infrared spectrum (Table II) was very similar to that of the Cu^{III} derivative, but the electronic spectrum in CH_3CN (Table III) was markedly different. The air-sensitive blue crystals were insoluble in water, but were soluble in common polar organic solvents. No suitable ^1H nmr spectrum of this compound could be obtained and an 80-MHz ^{11}B nmr in deuterioacetone consisted of two broad overlapping peaks of relative intensity 6:4 at +4.2 and +8.8 ppm relative to $BF_3 \cdot O(C_2H_5)_2$. Gouy balance measurements indicated the solid to have a magnetic moment of 1.8 BM, corresponding to one unpaired electron, as expected for a d^9 ion.

Cyclic voltammetry of either $[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10}-)_2]_2$ or $[(C_2H_5)_4N]_2Cu^{II}[(B_{10}C_2H_{10}-)_2]_2$ in dry CH_3CN with 0.1 M $(C_2H_5)_4NClO_4$ as supporting electrolyte (Table IV) gave a reversible wave at +0.15 V *vs.* sce for a reversible $Cu^{III}|Cu^{II}$ couple and an irreversible wave at −1.36 V *vs.* sce for an apparent $Cu^{II}|Cu^{I}$ couple followed by or involving decomposition of the reduced complex.

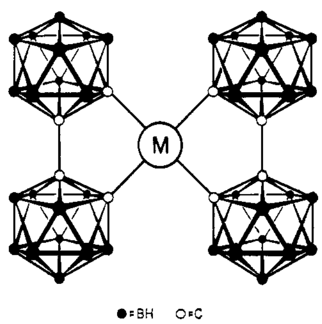

Figure 2. The proposed structure for the planar $M^{(4-n)+}[(B_{10}C_2H_{10}-)_2]_2^{n-}$ (M = Ni, Cu, n = 1, 2; M = Co, n = 1, 3) derivatives.

Preparation and Characterization of the Bis-σ,σ-2,2′-biscarboranyl–Nickel Complexes. When 2,2′-dilithiobiscarborane was stirred in anhydrous diethyl ether at the reflux temperature for 3 hr with 0.5 mol equiv of $NiBr_2 \cdot 2(CH_3OCH_2-)_2$,[16] an intensely colored red-brown oil was formed. Cation exchange and isolation as the tetraethylammonium salt afforded a 75% yield of orange-red diamagnetic plates of $[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2$, mp 259–262°. The infrared spectrum (Table II) contained a strong B–H stretching absorption at 2520 cm^{-1}, indicating anionic B–H groups. The spectrum was also marked by the absence of a typically strong C–H stretching absorbance at 3040 cm^{-1},[12] indicating the absence of any biscarborane C–H groups, and bands characteristic of the $(C_2H_5)_4N$ cation were present. The electronic spectrum in acetonitrile solution (Table III) gave only two strong bands in the visible and ultraviolet regions.

Table IV. Oxidation–Reduction Half-Wave Potentials *vs.* Sce in CH_3CN of the $[(C_2H_5)_4N]_nM^{(4-n)+}[(B_{10}C_2H_{10}-)_2]_2$ Derivatives[a]

M	$M^{III} + e^- \rightarrow M^{II}$	$M^{II} + e^- \rightarrow M^{I}$
Cu	+0.15[b]	−1.36[b,c]
Ni	+0.86[b]	−2.07[d]
Co	+0.62[b]	−2.35[d]
Zn		−2.36[d]

[a] M = Cu, Ni, Co, Zn; n = 1, 2, 3. [b] Measured by cyclic voltammetry with 0.1 M $(C_2H_5)_4NClO_4$ as supporting electrolyte. [c] Irreversible. [d] Measured with a dropping mercury electrode with 0.1 M $(C_2H_5)_4NClO_4$ as supporting electrolyte.

The complex did not form adducts with amines or phosphines. The orange-red crystals were stable to air for several weeks at a time, but acquired a brownish tinge when exposed for longer periods. Reaction of an acetone solution of the complex with dilute sulfuric acid gave 2 mol equiv of biscarborane/mol equiv of complex, and Ni^{II} ion was detected with dimethylglyoxime in the aqueous phase.

The 60-MHz ^1H nmr spectrum in deuterioacetone, as expected, exhibited only the resonances of the $(C_2H_5)_4N$ cation. The 32.1- and 77-MHz ^{11}B nmr spectra in acetone solution consisted of two sharp overlapping doublets centered at +7.2 ppm relative to $BF_3 \cdot O(C_2H_5)_2$.

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[16] R. B. King, Ed., "Organometallic Synthesis," Vol. I, Academic Press, New York, N. Y., p 72.

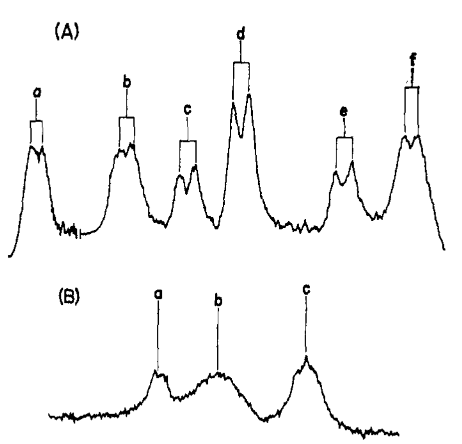

Figure 3. (A) A 77-MHz ^{11}B nmr of $\mathrm{Co^{III}[(B_{10}C_2H_{10}-)_2]_2^-}$ in acetone. Chemical shifts (coupling constants) are (a) −103.8 (124), (b) −15.6 (128), (c) −8.5 (142), (d) −2.5 (140), (e) +9.5 (144), (f) +17.2 (142) and are relative to external $\mathrm{BF_3 \cdot O(C_2H_5)_2}$. (B) An 80-MHz ^{11}B nmr of $\mathrm{Ni^{III}[(B_{10}C_2H_{10}-)_2]_2^-}$ in dichloromethane. Chemical shifts are (a) −14.2, (b) −4.4, (c) +11.0 and are relative to external $\mathrm{BF_3 \cdot O(C_2H_5)_2}$.

From the infrared and nmr data, which indicated that the product was a diamagnetic anion containing only B–H and no C–H units of biscarborane, and from the observed diamagnetism and electronic spectrum, which indicated that the metal ion was planar $\mathrm{Ni^{II}}$ (d^8), we proposed[13] the structure presented in Figure 2 for $\mathrm{[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2}$, with the nickel atom of the complex σ bonded to the four carbon atoms of the two biscarborane units. A pseudotetrahedral (high-spin) configuration was ruled out because of the color and diamagnetic properties of the complex.

When $\mathrm{[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2}$ was stirred in dry dichloromethane with a large excess of anhydrous cupric chloride for 4 hr, the orange-red color of $\mathrm{Ni^{II}[(B_{10}C_2H_{10}-)_2]_2^{2-}}$ disappeared and the deep green color of $\mathrm{Ni^{III}[(B_{10}C_2H_{10}-)_2]_2^-}$ developed

$$\mathrm{Ni^{II}[(B_{10}C_2H_{10}-)_2]_2^{2-} + CuCl_2 \xrightarrow{CH_2Cl_2} Ni^{III}[(B_{10}C_2H_{10}-)_2]_2^- + CuCl + Cl^-}$$

Filtration and fractional crystallization of the filtrate gave, in 73% yield, bright green paramagnetic needles of $\mathrm{[(C_2H_5)_4N]Ni^{III}[(B_{10}C_2H_{10}-)_2]_2}$, mp 178–181° dec. The infrared spectrum (Table II) was very similar to that of the $\mathrm{Ni^{II}}$ derivative. The electronic spectrum obtained in $\mathrm{CH_3CN}$ (Table III), however, was markedly different and more complex than that of the corresponding $\mathrm{Ni^{II}}$ derivative, as expected for a change from a d^8 ion to a planar d^7 ion. The complex was insoluble in water and nonpolar organic solvents, but was very soluble in all of the common polar organic solvents. In wet dichloromethane it oxidized triphenylphosphine to triphenylphosphine oxide

$$\mathrm{(C_6H_5)_3P + 2Ni^{III}[(B_{10}C_2H_{10}-)_2]_2^- + H_2O \xrightarrow{CH_2Cl_2} (C_6H_5)_3PO + 2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2^{2-} + 2H^+}$$

This $\mathrm{Ni^{III}}$ derivative was stable to dry air indefinitely, but very slowly decomposed in moist air to give some $\mathrm{Ni(OH)_2}$, biscarborane, and some $\mathrm{Ni^{II}[(B_{10}C_2H_{10}-)_2]_2^{2-}}$.

The 60-MHz ^{1}H nmr and 32.1-MHz ^{11}B nmr spectra in acetone consisted of rather broad resonances which were not interpreted. The 80-MHz ^{11}B nmr spectrum in $\mathrm{CH_2Cl_2}$ (Figure 3) consisted of three broad resonances centered at −14.2, −4.4, and +11.0 ppm. Their relative intensities were 2:4:4, respectively, and accounted nicely for the ten boron atoms in each polyhedron in the complex. The resonance of total intensity 2 at low field, a, was assigned with some confidence to boron atoms 3 and 6 (Figure 1) of each polyhedron, since these boron atoms are nearest the metal atom and would be expected to be shifted to low field by the electron-deficient Ni atom. The other two resonances were not specifically assigned.

Gouy balance measurements indicated the magnetic moment of solid $\mathrm{[(C_2H_5)_4N]Ni^{III}[(B_{10}C_2H_{10}-)_2]_2}$ to be 1.7 BM, corresponding to a single unpaired electron and low-spin $\mathrm{Ni^{III}}$ (d^7). This low-spin d^7 ion would be the electronic configuration expected for planar $\mathrm{Ni^{III}}$. We therefore proposed the structure shown in Figure 2 for $\mathrm{[(C_2H_5)_4N]Ni^{III}[(B_{10}C_2H_{10}-)_2]_2}$.

Cyclic voltammetry of either $\mathrm{[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2}$ or $\mathrm{[(C_2H_5)_4N]Ni^{III}[(B_{10}C_2H_{10}-)_2]_2}$ in acetonitrile with 0.1 *M* $\mathrm{(C_2H_5)_4NClO_4}$ as supporting electrolyte gave a reversible one-electron wave at +0.86 V *vs.* sce for the $\mathrm{Ni^{III}|Ni^{II}}$ couple (Table IV). Polarography with a dropping mercury electrode gave a reversible one-electron reduction wave at −2.07 V *vs.* sce for the $\mathrm{Ni^{II}|Ni^{I}}$ couple.

Preparation and Characterization of the Bis-σ,σ-2,2′-biscarboranyl–Cobalt Complexes. When 2,2′-dilithiobiscarborane was stirred in anhydrous diethyl ether at the reflux temperature for 3 hr with 0.5 mol equiv of anhydrous $\mathrm{CoCl_2}$, an oily purple solid formed

$$\mathrm{2Li_2(B_{10}C_2H_{10}-)_2 + CoCl_2 \xrightarrow{(C_2H_5)_2O} Li_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2 + 2LiCl}$$

Isolation as the tetraethylammonium salt afforded a 76% yield of long pale purple paramagnetic needles of $\mathrm{[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2}$, mp 275–277° dec. The infrared spectrum (Table II) was very similar to that of the copper and nickel derivatives, except that more bands were seen in the 700–900-cm^{-1} region. The strong absorbance at 2550 cm^{-1} was assigned, as before, to anionic B–H groups. The spectrum was also typically marked by the absence of any carborane C–H stretching bands and bands characteristic of the $\mathrm{(C_2H_5)_4N}$ cation were present. The electronic spectrum in acetonitrile (Table III) consisted of several maxima in the visible and ultraviolet regions.

The complex did not form adducts with carbon monoxide, nitric oxide, amines, or phosphines. The purple crystals were stable indefinitely to moist air, and could be recovered unchanged after heating in water at 100° for 24 hr. Reaction of an acetone solution of the complex with concentrated hydrochloric acid gave 2 mol equiv of biscarborane/mol equiv of complex, and $\mathrm{Co^{II}}$ was identified as the deep blue $\mathrm{CoCl_4^{2-}}$ ion.

The 60-MHz ^{1}H nmr spectrum of the tetraphenylarsonium salt in dichloromethane consisted of only broad resonances for solvent and cation protons. No 32.1- or 80-MHz ^{11}B nmr spectra could be obtained, and Gouy balance measurements indicated the magnetic moment of solid $\mathrm{[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2}$ to be 4.1 BM, corresponding to three unpaired electrons and a high-spin $\mathrm{Co^{II}}$(d^7) atom. From this magnetic moment and the color of the complex, we proposed the structure in Figure 4, for $\mathrm{[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2}$, wherein the polyhedra of two biscarborane units are in a pseudotetrahedral configuration, with the four carbon atoms of one biscarborane unit in a plane perpendicular to the plane containing the four carbon atoms of the second biscarborane unit. This pseudotetrahedral configuration would be the one expected for any high-spin d^7 or d^8 ions.

When $[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$ was stirred in dry dichloromethane with a large excess of anhydrous cupric chloride for 4 hr, the purple color of the Co^{II} derivative disappeared and the intensely dark red-brown color of the Co^{III} derivative developed

$$\mathrm{Co^{II}[(B_{10}C_2H_{10}-)_2]_2{}^{2-} + CuCl_2 \xrightarrow{CH_2Cl_2} Co^{III}[(B_{10}C_2H_{10}-)_2]_2{}^{-} + CuCl + Cl^-}$$

Filtration and fractional crystallization of the filtrate gave, in 83% yield, black, diamagnetic needles of $[(C_2H_5)_4N]Co^{III}[(B_{10}C_2H_{10}-)_2]_2$, mp 195-196° dec. The infrared spectrum (Table II) was very similar to those of the other derivatives. The electronic spectrum in acetonitrile (Table III), however, was quite different from that of the Co^{II} derivative, and consisted of a tail marked by shoulders throughout most of the visible and ultraviolet region.

The complex was insoluble in water and nonpolar organic solvents, but was extremely soluble in diethyl ether, dichloromethane, and the other common polar organic solvents. It did not react with dry amines or phosphines. The complex reacted with tetraethylammonium iodide in aqueous ethanol to give the Co^{II} derivative and elemental iodine.

$$\mathrm{2(C_2H_5)_4NI + 2[(C_2H_5)_4N]Co^{III}[(B_{10}C_2H_{10}-)_2]_2 \xrightarrow{H_2O,\ C_2H_5OH} 2[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2 + I_2}$$

The solid Co^{III} complex was stable to dry air indefinitely, but solutions of it slowly decomposed when exposed to moist air for extended periods of time, giving sizable amounts of the Co^{II} derivative.

The 60-MHz ^1H nmr spectrum in deuterioacetone, as expected, exhibited only the resonances of the $(C_2H_5)_4N$ cation.

The 77-MHz ^{11}B nmr spectrum [relative to $BF_3 \cdot O(C_2H_5)_2$] in acetone (Figure 3) consisted of six discrete doublets at +17.2 (J = 131), +9.5 (J = 144), −2.5 (J = 140), −8.5 (J = 142), −15.6 (J = 128), and −103.8 (J = 124), of relative intensities 2:1:2:1:2:2, respectively. The doublet of intensity 2 at extremely low field (a) was assigned to the 3 and 6 boron atoms of each polyhedron (Figure 1), the pair within bonding distance of the electron-withdrawing Co^{III} atom and bonded to both of the carbon atoms. The doublet of intensity 2 at −15.6 (b) was assigned to the equivalent 7 and 11 boron atoms, which are close to the metal atom but bound to only one of the two carbon atoms, the carbon atoms directly bonded to the metal atom. The doublet of intensity 1 at −8.5 ppm (c) was assigned to the unique 12 boron atom, which is the closest of the two unique boron atoms to the electron-withdrawing Co^{III} atom. The doublet of intensity 2 at −2.5 ppm (d) was assigned to the 4 and 5 boron atoms, the pair of equivalent boron atoms bound to the carbon atom 1, the carbon atom not bound to the metal atom. The sharp doublet of intensity 1 at +9.5 ppm (e) was assigned to the unique 9 boron atom, which is the boron atom farthest from the metal atom and least affected by it. The high-field doublet at +17.2 ppm (f) was assigned to the 8 and 10 boron atoms, the equivalent pair of boron atoms bound to neither carbon nor to the Co^{III} atom. This pair of boron atoms should carry the highest electron density.

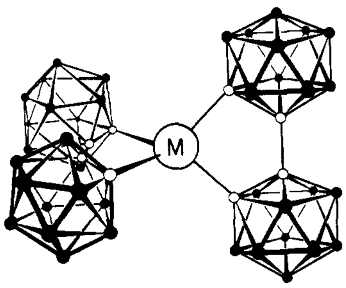

Figure 4. The proposed structure for the pseudotetrahedral $M^{(4-n)+}[(B_{10}C_2H_{10}-)_2]_2{}^{n-}$ (M = Co, Zn; n = 2) derivatives.

From this nmr data and the diamagnetism of the complex, we proposed that $[(C_2H_5)_4N]Co^{III}[(B_{10}C_2H_{10}-)_2]_2$ has the planar structure shown in Figure 2, the expected configuration for a low-spin d^6 ion.

When $[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$ was stirred in dry acetonitrile in an evacuated system with an excess of 0.5% lithium amalgam for 2 hr, the initially purple solution turned red-brown.

$$\mathrm{Co^{II}[(B_{10}C_2H_{10}-)_2]_2{}^{2-} + Li(Hg) \xrightarrow{CH_3CN} Co^{I}[(B_{10}C_2H_{10}-)_2]_2{}^{3-} + Li^+ + Hg}$$

The Co^I salt could not be isolated in a pure state; exposure to even minute amounts of moisture of air caused regeneration of the purple Co^{II} derivative in quantitative yield. This acetonitrile solution could, however, after filtration to remove excess amalgam, be made to induce coupling reactions with alkyl halides; the addition of 1 mol equiv of dry methyl iodide caused immediate and quantitative formation of the Co^{II} derivative and simultaneous evolution of ethane, which was collected and identified by means of its mass spectrum. Reaction of 1 mol equiv of the Co^I derivative in acetonitrile solution with 1 mol equiv of dry benzyl bromide gave a quantitative yield of the Co^{II} derivative and a 52% isolated yield of 1,2-diphenylethane

$$\mathrm{2Co^{I}[(B_{10}C_2H_{10}-)_2]_2{}^{3-} + 2CH_3I \xrightarrow{CH_3CN} 2Co^{II}[(B_{10}C_2H_{10}-)_2]_2{}^{2-} + C_2H_6 + 2I^-}$$

$$\mathrm{2Co^{I}[(B_{10}C_2H_{10}-)_2]_2{}^{3-} + C_6H_5CH_2Br \xrightarrow{CH_3CN} 2Co^{II}[(B_{10}C_2H_{10}-)_2]_2{}^{2-} + (C_6H_5CH_2-)_2 + 2Br^-}$$

These reactions of this $Co^I[(B_{10}C_2H_{10}-)_2]_2{}^{3-}$ derivative were strikingly reminiscent of reactions of certain of the cobalamine complexes prepared by Schrauzer, *et al.*,[17,18] to which it is formally analogous. In the cobalamine system, however, the $Co^{II}|Co^I$ couple is more accessible than in the analogous bis-σ,σ-2,2′-biscarboranyl–cobalt system, and stable alkylated cobalamine complexes are formed. No stable alkylated derivatives of the Co^I–$[(B_{10}C_2H_{10}-)_2]_2{}^{3-}$ system were formed.

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(17) G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968).

(18) G. N. Schrauzer, J. W. Sibert, and R. J. Windgassen, *J. Amer. Chem. Soc.*, 90, 6681 (1968).

Cyclic voltammetry in acetonitrile solutions (Table IV) of either $[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$ or $[(C_2H_5)_4N]Co^{III}[(B_{10}C_2H_{10}-)_2]_2$ with 0.1 *M* $(C_2H_5)_4NClO_4$ as supporting electrolyte gave a reversible wave at +0.62 V *vs.* sce for the $Co^{III}|Co^{II}$ couple. Reduction of $Co^{II}[(B_{10}C_2H_{10}-)_2]_2^{2-}$ with a dropping mercury electrode gave a reduction wave at −2.35 V *vs.* sce for the $Co^{III}|Co^{I}$ couple.

Preparation and Characterization of Bis-σ,σ-2,2′-biscarboranylzinc. Treatment of a diethyl ether slurry of 2,2′-dilithiobiscarborane with 0.5 mol equiv of anhydrous $ZnCl_2$, followed by cation exchange and isolation of the white product as the tetraethylammonium salt, afforded an 85% yield of $[(C_2H_5)_4N]_2Zn^{II}[(B_{10}C_2H_{10}-)_2]_2$, mp 227–231° dec. The infrared spectrum (Table II) was nearly identical with that of the Co^{II} derivative. The electronic spectrum in CH_3CN (Table III) consisted of a sharp absorption with a small shoulder in the ultraviolet region.

The complex was insoluble in water, diethyl ether, and nonpolar organic solvents, soluble in dichloromethane and acetonitrile, and soluble with decomposition in acetone and alcohols. The complex did not form adducts with amines or phosphines. The white crystals were stable indefinitely to dry air and slowly decomposed in moist air to give $Zn(OH)_2$ and biscarborane. Reaction of an acetone solution of the complex with HCl gave 2 mol equiv of biscarborane/mol equiv of complex, and Zn^{II} was identified by precipitation with H_2S.

The 60-MHz ^1H nmr spectrum of $[(C_2H_5)_4N]_2Zn^{II}[(B_{10}C_2H_{10}-)_2]_2$ in acetonitrile showed only the resonances of the $(C_2H_5)_4N^+$ cation. The 32.1-MHz ^{11}B nmr spectrum consisted of a set of overlapping doublets centered at +7.4 ppm [relative to $BF_3 \cdot O(C_2H_5)_2$]. Polarography with a dropping mercury electrode (Table IV) showed a reversible one-electron wave at −2.36 V *vs.* sce, corresponding to either a $Zn^{II}|Zn^{I}$ couple or to a one-electron ligand reduction.

From the similarity of the infrared spectrum to that of the Co^{II} derivative and the fact that the crystals of both salts appeared to be isomorphous we propose that the Zn^{II} derivative has the pseudotetrahedral structure shown in Figure 4, the same gross structure proposed for the Co^{II} derivative.

Conclusion

The unusual air and water stability exhibited by the carbon–metal σ bonds in these complexes can be attributed to a combination of several mutually beneficial factors. First, the carbon atoms bound to the metal are parts of extremely bulky polyhedra and tend to make further substitution reactions at carbon or metal impossible. The strong Coulombic interaction of the highly charged central metal ions and divalent 2,2′-biscarboranyl ligands further stabilize the system. Lastly, the number of accessible and interconvertible oxidation states exemplifies the stabilization of these complexes, with the four large polyhedra in each complex acting as large electron reservoirs or electron sinks. For these reasons, the possibility of combining these unusual 2,2′-biscarboranyl ligands with other transition metal ions, transition metal carbonyls, and main group elements appears fruitful, and preliminary studies of certain of these systems are underway.

Experimental Section

Methods and Materials. The majority of solvents and chemicals used were of reagent grade, and were used without further purification. Ethyl ether was further purified by distillation from lithium aluminum hydride, while dichloromethane was further purified by distillation from phosphorus pentoxide. Zinc chloride and cupric chloride were Matheson Coleman and Bell reagent grade and were used with further purification. Anhydrous cobalt chloride was prepared by heating the hexahydrate under high vacuum at 140° for 48 hr. Nickel bromide was prepared by the method of King[16] and was washed with ethyl ether immediately before use. *n*-Butyllithium was supplied by Foote Chemical Co. and was used without further purification. Biscarborane {1-[1′-1′,2′-dicarba-*closo*-dodecaborane(12)]-1,2′-dicarba-*closo*-dodecaborane(12)} was prepared by literature methods.[12] All reactions involving biscarborane and its derivatives were carried out under nitrogen atmospheres. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer Model 137 sodium chloride spectrometer. Proton nmr spectra were obtained using a Varian A-60 spectrometer, while 32.1-MHz ^{11}B nmr spectra were obtained using a Varian HA-100 spectrometer and 77- and 80-MHz ^{11}B nmr spectra were obtained using an experimental nmr spectrometer developed by Professor F. A. L. Anet. Sample concentrations for both nmr spectra were 10–50%. Melting points were determined using a Thomas-Hoover capillary melting point apparatus. Osmometric molecular weights and elemental analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

$[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10}-)_2]_2$. In a 500-ml three-necked round-bottom flask equipped with a magnetic stirrer, a pressure-equalizing addition funnel, a stopper, and a Dry Ice condenser topped with a nitrogen inlet were placed 250 ml of anhydrous ethyl ether, a magnetic stirring bar, and 5.74 g (20 mmol) of biscarborane $[1-(1'-1',2'-B_{10}C_2H_{11})-1,2-B_{10}C_2H_{11}]$. In the addition funnel was placed 20 ml (40 mmol) of 2 *N* *n*-butyllithium in hexane, which was allowed to drip slowly into the stirring reaction mixture at reflux. After all the *n*-butyllithium had been added, the reaction mixture was refluxed for 1 hr. An ethyl ether slurry of 2.7 g (20.2 mmol) of anhydrous $CuCl_2$ was then added and the reaction mixture was stirred and refluxed for 3 hr. The reaction mixture was cooled and the ethyl ether and hexane were rotary evaporated from it. A solution of 2.1 g (10 mmol) of $(C_2H_5)_4NBr$ in 100 ml of dry CH_2Cl_2 was added to the solid with vigorous stirring. Filtration of the resulting mixture gave a yellow solution, which was rotary evaporated onto 25 g of 200-mesh silica gel, and a yellow band was eluted from a 9-in. column of silica gel with 500 ml of dry 1:1 ethyl ether–dichloromethane. Slow rotary evaporation of the eluent at room temperature gave 4.1 g (5.4 mmol, 54%) of yellow diamagnetic crystalline $[(C_2H_5)_4N]Cu^{III}[B_{10}C_2H_{10}-)_2]_2$, mp 210–212°. The 32.1-MHz ^{11}B nmr spectrum in CH_3CN showed overlapping doublets centered at +3.9 and −0.5 ppm. The 60-MHz ^1H nmr spectrum in deuterioacetone exhibited cation resonances centered at τ 8.60 (triplet of triplets, intensity 3) and 6.52 (quartet, intensity 2). Analytical data and the infrared and electronic spectra are presented in Tables I, II, and III.

$[(C_2H_5)_4N]_2Cu^{II}(B_{10}C_2H_{10}-)_2]_2$. Lithium Reduction Method. In a 100-ml filter flask with a nitrogen inlet were placed a magnetic stirring bar, 25 ml of dry acetone, 0.42 g (2 mmol) of $(C_2H_5)_4NBr$, and 1.53 g (2 mmol) of $[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10})_2]_2$. Lithium, 0.1 g (14 mg-atoms), was added; the flask was stoppered and stirred for 3 hr. The color changed from yellow to blue. Ethyl ether, 75 ml, was added and the resulting mixture was quickly filtered under a stream of nitrogen into a 500-ml filter flask, which was then equipped with a nitrogen inlet. To the filtrate, with vigorous stirring, was added slowly 200 ml of pentane. Blue needles of $[(C_2H_5)_4N]_2Cu^{II}[(B_{10}C_2H_{10}-)_2]_2$, mp 221–223° dec, 0.98 g (1.1 mmol), were obtained in 55% yield. Analytical data and the infrared and electronic spectra are presented in Tables I, II, and III.

$[(C_2H_5)_4N]_2Cu^{II}[(B_{10}C_2H_{10}-)_2]_2$. Zinc Reduction Method. In a 250-ml round-bottom flask equipped with a nitrogen inlet, a magnetic stirring bar, and a stopper were placed 2 g of mossy zinc, 80 ml of dry dichloromethane, 0.42 g (2 mmol) of $(C_2H_5)_4NBr$, and 1.53 g (2 mmol) of $[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10}-)_2]_2$. The reaction mixture was stirred vigorously at room temperature for 4 hr, and the resulting blue mixture was filtered under a nitrogen atmosphere into a 250-ml suction filter flask. Ethyl ether–acetone (150 ml, 14:1) was added, and the resulting mixture was filtered into a 500-ml suction filter flask. To the filtrate, with vigorous sitrring, was added slowly 200 ml of dry pentane. Deep blue needles of $[(C_2H_5)_4N]_2Cu^{II}[(B_{10}C_2H_{10}-)_2]_2$, mp 221–223° dec, formed and were isolated by suction filtration under nitrogen. The yield was 1.43 g (1.6 mmol, 80%).

$[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2$. In a 500-ml three-necked round-bottom flask equipped with a mechanical stirrer, a pressure-equalization addition funnel, and a Dry Ice condenser topped by a nitrogen inlet were placed 200 ml of anhydrous ethyl ether and 8.61 g (30 mmol) of biscarborane. In the addition funnel was placed 28 ml (64.4 mmol) of 2.3 *N* *n*-butyllithium in hexane. The *n*-butyllithium was added slowly and the reaction mixture was refluxed for 1 hr. In the addition funnel were then placed 8 g (20 mmol, 50% excess) of $NiBr_2 \cdot 2(CH_3OCH_2-)_2$[16] and 50 ml of anhydrous ethyl ether. This slurry was added all at once to the reaction mixture, and an intense red-brown oil formed in the reaction flask. The reaction mixture was stirred and refluxed for 3 hr and cooled, and the supernatant ether layer was decanted. To the lower layer was added a solution of 8.4 g (40 mmol, 33% excess) of $(C_2H_5)_4NBr$ in 200 ml of CH_2Cl_2. The mixture was stirred for 0.5 hr and then was filtered. To the filtrate at −10° was added 200 ml of anhydrous ethyl ether. An orange-brown solid separated, which was collected and washed on the filter with a total of 1000 ml of water. The resulting orange solid was recrystallized from approximately 100 ml of boiling CH_2Cl_2. Two fractions yielded 9.7 g (11 mmol, 73%) of diamagnetic red-orange blocks of $[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2]_2$, mp 259–262°. The 32.1-MHz ^{11}B nmr spectrum in acetone contained overlapping doublets centered at +7.2 ppm. The 60-MHz ^1H nmr spectrum in deuterioacetone consisted of cation resonances at τ 8.63 (triplet, intensity 3) and at τ 6.51 (quartet, intensity 2). Analytical data and the infrared and electronic spectra are presented in Tables I, II, and III.

$[(C_2H_5)_4N]Ni^{III}[(B_{10}C_2H_{10}-)_2]_2$. In a 500-ml round-bottom flask equipped with a nitrogen inlet was placed a magnetic stirring bar and 250 ml of dry CH_2Cl_2. $[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}-)_2$, 7 g (7.9 mmol), was added and stirring was begun. Anhydrous $CuCl_2$, 25 g, was added and the reaction mixture was stirred for 4 hr. The reaction mixture was filtered through a medium-porosity sintered glass frit and to the filtrate was added 100 ml of dry hexane. The resulting mixture was filtered and the resulting filtrate was rotary evaporated at room temperature to approximately 50 ml. The green crystalline solid was collected and afforded 4.6 g (6 mmol, 76%) of $[(C_2H_5)_4N]Ni^{III}[(B_{10}C_2H_{10}-)_2]_2$, mp 178–181°. Analytical data and the infrared and electronic spectra are presented in Tables I, II, and III.

$[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$. In a 500-ml three-necked, round-bottom flask equipped with a mechanical stirrer, a pressure-equalizing addition funnel, a stopper, and a Dry Ice condenser topped by a nitrogen inlet, was placed 8.61 g (30 mmol) of biscarborane and 200 ml of anhydrous ethyl ether. In the addition funnel was placed 27 ml (62 mmol) of 2.3 *N* *n*-butyllithium in hexane, which was added slowly over a 0.5-hr period with reflux. After reflux for 1.5 hr, a slurry of 2.34 g (18 mmol) of anhydrous $CoCl_2$ in 50 ml of anhydrous ethyl ether was added, and the reaction mixture was refluxed and stirred for 3 hr. The reaction mixture was cooled, and the supernatant ether layer was decanted, and 2 ml of water was added to the ether layer. Rotary evaporation of this layer, followed by vacuum sublimation at 150°, afforded 0.8 g (2.8 mmol, 9%) of biscarborane. To the purple oily solid left in the reaction flask was added a solution of 6.8 g (32 mmol) of $(C_2H_5)_4NBr$ in 200 ml of dry dichloromethane. The mixture obtained was stirred for 0.5 hr, and 200 ml of ethyl ether was added. The purple precipitate so obtained was collected and washed with 500 ml of ethyl ether and 500 ml of distilled water. The complex was recrystallized from 200 ml of boiling 1:20 acetone–dichloromethane. Two fractions yielded 10.03 g (11.3 mmol, 75%) of long purple needles of $[(C_2H_5)_4]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$, mp 275–277° dec. The magnetic moment of the solid was found to be 4.1 BM. The 60-MHz ^1H nmr spectrum in deuterioacetone showed broad paramagnetic cation and solvent resonances. No ^{11}B nmr of the paramagnetic complex could be obtained. Analytical data and the infrared and electronic spectra are presented in Tables I, II, and III.

$[(C_2H_5)_4N]Co^{III}[(B_{10}C_2H_{10}-)_2]_2$. In a 500-ml one-necked round-bottom flask were placed a magnetic stirring bar and 25 g of anhydrous $CuCl_2$. Solid $[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$, 3.36 g (3.78 mmol), was added to the reaction flask along with 250 ml of dry CH_2Cl_2. The reaction mixture was stirred for 4 hr at room temperature under a nitrogen atmosphere. The reaction mixture was then filtered through a thoroughly dried sintered glass frit. The precipitate was washed with two 25-ml portions of dry CH_2Cl_2 and the combined filtrates were rotary evaporated at room temperature to a volume of approximately 30 ml. Anhydrous ethyl ether was added at the boiling point until precipitation begun. The solution was filtered and the frit was washed with two 1-ml portions of dry CH_2Cl_2. The combined filtrates were warmed to dissolve all of the complex, and this solution was allowed to cool slowly to room tempeature and was then placed in an ice–water bath. Black needles of diamagnetic $[(C_2H_5)_4N]Co^{III}[(B_{10}C_2H_{10}-)_2]_2$, mp 195–196° dec, 2.38 g (3.14 mmol, 83%), were obtained. The 60-MHz ^1H nmr in deuterioacetone consisted of cation resonances at τ 8.56 (triplet, intensity 3) and 6.47 (quartet, intensity 2). The 77-MHz ^{11}B nmr spectrum in acetone consisted of six discrete doublets of intensities 2:2:1:2:1:2, respectively, ranging from −103.8 to +17.2 ppm. Analytical data and the infrared and electronic spectra are presented in Tables I, II, and III.

$Co^{I}[(B_{10}C_2H_{10}-)_2]_2^{3-}$. In a rigorously dried 250-ml Schlenk flask equipped with a high-vacuum nitrogen inlet were placed a magnetic stirring bar and 12 g (8.5 mmol) of a 0.5% lithium amalgam. Solid dry $[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$, 0.89 g (1 mmol), was also placed in the flask. The flask was connected to a high-vacuum adapter to which was also fitted a Schlenk filter connected to a second Schlenk flask containing a magnetic stirring bar. The system was evacuated and 50 ml of CH_3CN was vacuum distilled from CaH_2 into the reaction flask, which was kept cooled at −196°. The reaction flask was then warmed to room temperature and the resulting purple mixture was stirred for 2 hr. The color changed to the red-brown color of $Co^{I}[(B_{10}C_2H_{10}-)_2]_2^{3-}$, and the reaction mixture was Schlenk filtered into the second flask. No residue other than lithium amalgam was observed on the frit. The salt could not be isolated; exposure to even minute amounts of oxygen or moisture caused regeneration of the purple $Co^{II}[(B_{10}C_2H_{10}-)_2]_2^{2-}$ ion in nearly quantitative yield.

Reaction of $Co^{I}[(B_{10}C_2H_{10}-)_2]_2^{3-}$ with CH_3I. A Co^{I} solution as prepared above was cooled to −196°, and 0.14 g (1 mmol) of CH_3I in 10 ml of anhydrous ethyl ether was vacuum distilled into the cooled flask. Warming the reaction mixture to room temperature with stirring caused gas evolution and formation of the purple color of Co^{II}. The gas was trapped in a mass spectra sampling tube and the mass spectrum of the trapped gases showed ethane to be the principal component. Ethyl ether and methylamine were also detected. The reaction mixture was rotary evaporated to near dryness and was recrystallized from 20 ml of CH_2Cl_2 to which 1 ml of acetone was added at boiling. The yield of $[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$, identified by means of its infrared spectrum, color, and crystal habit, was 0.82 g (0.92 mmol, 92%).

Reaction of $Co^{I}[(B_{10}C_2H_{10}-)_2]_2^{3-}$ with $C_6H_5CH_2Br$. A Co^{I} solution as prepared above was cooled to −196° and 0.17 g (1 mmol) of $C_6H_5CH_2Br$ was vacuum distilled into the cooled reaction flask. Warming the reaction flask to room temperature with stirring caused immediate formation of the purple color of Co^{II}. The reaction mixture was rotary evaporated onto 10 g of silica gel and two fractions were eluted from a 9-in. silica gel column. Elution with 300 ml of dry ethyl ether gave, after rotary evaporation of the ether, 80 mg of crude organic material. Recrystallization of this product from 5 ml of hexane at −50° afforded 47 mg (0.26 mmol, 52%) of $C_6H_5CH_2CH_2C_6H_5$, identified by comparison of its infrared spectrum with that of a known sample. Elution with 100 ml of acetone, rotary evaporation, and recrystallization of the purple residue from 20 ml of boiling 1:20 acetone–dichloromethane gave 0.84 g (0.94 mmol, 94%) of $[(C_2H_5)_4N]_2Co^{II}[(B_{10}C_2H_{10}-)_2]_2$, identified by means of its infrared spectrum, color, and crystal habit.

$[(C_2H_5)_4N]_2Zn^{II}[(B_{10}C_2H_{10}-)_2]_2$. In a 100-ml three-necked round-bottom flask equipped with a magnetic stirrer, a nitrogen inlet, and a stopper were placed 60 ml of anhydrous ethyl ether, 2.87 g (10 mmol) of biscarborane, and a magnetic stirring bar. Stirring was begun and 12.5 ml of 1.6 *N* *n*-butyllithium in hexane was added over a 3-min period by means of a syringe. The reaction mixture was stirred for 1 hr and 0.69 g (5 mmol) of anhydrous $ZnCl_2$ was added all at once. The reaction mixture was stirred for an additional 3 hr, during which time a white solid precipitated on the sides of the reaction flask. Under a stream of nitrogen, the supernatant ether layer was decanted and 80 ml of dry dichloromethane was added to the solid in the reaction flask. The resulting mixture was stirred for 0.5 hr and was then filtered under a nitrogen atmosphere into a 250-ml suction filter flask, which was immediately equipped with a nitrogen inlet. A solution of 2.1 g (10 mmol) of $(C_2H_5)_4NBr$ in 30 ml of dry dichloromethane was added slowly and a white precipitate began to form in the flask. Addition of 100 ml of anhydrous ethyl ether completed precipitation. The resulting white precipitate was collected by suction filtration under a nitrogen atmosphere and was recrystallized from 85 ml of hot dichloromethane to which 20 ml of ethyl ether was added at boiling. Long white needles of $[(C_2H_5)_4N]_2Zn^{II}[(B_{10}C_2H_{10}-)_2]_2$, mp 227–231° dec, were collected. The yield was 3.80 g (4.25 mmol, 85%). The 60-MHz ^1H nmr spectrum in deuterioacetone consisted of a triplet of triplets of intensity 3 at τ 8.59 (J = 7.1, J' = 1.8) and a quartet of intensity 2 at τ 6.50 (J = 7.1), corresponding to the cation methyl and methylene protons, respectively. The 32.1-MHz ^{11}B nmr spectrum consisted of a set of overlapping doublets centered at +7.4 ppm. Analytical data and the infrared and electronic spectra are presented in Tables I, II, and III.

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Addition Reactions on Coordinated Olefinic Ligands. IV. Stereoselective Synthesis between Dichloro(1,5-hexadiene)platinum(II) and Enantiomeric (*S*)-α-Methylbenzylamine[1]

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Abstract: Interaction between dichloro(1,5-hexadiene)platinum(II) and (*S*)-α-methylbenzylamine has been investigated. The addition reaction leads to a derivative containing a carbon–platinum σ bond. It is possible to obtain an equimolar mixture of two diastereoisomeric forms, or a single one, depending on reaction conditions. The reaction involving the formation of binuclear products from the crude diastereoisomeric mixture has been found to be highly stereoselective. Circular dichroism spectra of monomeric and binuclear products are discussed.

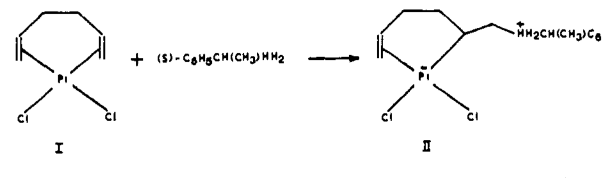
In a previous report[2] we described the addition reactions of ammonia and aliphatic amines on diene complexes of Pt(II) and Pd(II). Such reactions, as well as the ones involving the addition of other nucleophiles, follow a stereospecific mechanism.[3,4] Furthermore, in cases where optically active reagents were present, it was possible to find some stereoselectivity.

Indeed, enantiomeric complexes of disymmetric olefins, as (+)-dichloro(*endo*-dicyclopentadiene)platinum(II) and (−)-dichloro(*endo*-dicyclopentadiene)palladium(II), react with *dl*-*sec*-butyl alcohol[5] in the presence of bases in a quite stereospecific way, showing a stereoselectivity of about 10–20%. A still higher stereoselectivity was also found[6] in the reaction between the racemic complex dichloro(4-vinylcyclohexene)platinum(II) and (*S*)-α-methylbenzylamine.

In this paper we report the reaction between an optically active nucleophilic agent, (*S*)-α-methylbenzylamine, and a Pt(II) complex with a prochiral diene (that is, having prochiral[7] or enantiotopic[8] faces), dichloro(1,5-hexadiene)platinum(II) (I, Figure 1). The organic moiety of this complex is coordinated to the metal so that carbon atoms C-2 and C-5 are opposite in configuration. That is the same as saying that both the enantiotopic faces of a double bond are coordinated to the same metal atom. The results of the X-ray crystal structure analysis of the analogous Pd(II) complex[9] support our assumptions.

The choice of such a substrate was suggested in order to extend our previous investigations[10] on the molecular asymmetry in prochiral olefins and transition metal complexes. This substrate enables us to study the possible stereochemical features of processes involving some stereospecificity and stereoselectivity (*e.g.*, biological and enzymatic reactions, stereospecific polymerization, etc.) on a simple molecular model.

The addition reaction of (*S*)-α-methylbenzylamine to complex I (eq 1) can yield either two diastereoisomeric forms, or a single one, according to the reaction conditions. The crude mixture (II) of the two diastereoisomers, obtained *via* eq 1, can react further (eq 2)



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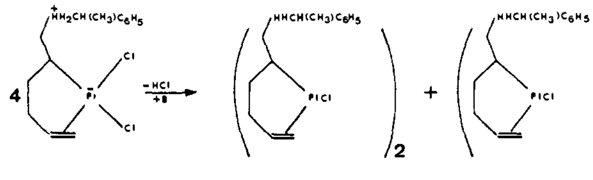

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