borane icosahedron is essentially identical with that of the carbon atoms.

Finally, it is worth noting that the quadrupole splitting in IV is nearly the same as that reported[13] for $(\pi\text{-}C_5H_5)_2Fe^+BF_4^-$ (0.65 mm/sec at 80°K, 0.76 mm/sec at 298°K), while the unresolved splitting in III cannot be significantly different from that in II [a value <0.1 mm/sec was reported earlier[14]]. These data suggest very strongly that while the major contribution to $^1/_2e^2qQ$ originates in the departure from cubic symmetry of the metal orbitals (primarily 3d), smaller contributions arising from distorting by steric effects of the bonding orbitals directed toward the ligands must be included in a quantitative consideration of the field gradient tensor at the iron atom lattice point. However, since the reported differences in the quadrupole splitting parameters of the BF_4^- and ClO_4^- ferrocene derivatives differ by only 2% of the splitting in the parent ferrocene molecule and are barely outside the reported errors of the individual measurements, such differences can be safely neglected in the qualitative considerations of the present discussion.

Unfortunately, the chemical aftereffects of the electron-capture decay in ^{57}Co preclude an estimate of the similarity (or difference) between $(\pi\text{-}C_5H_5)_2Co^+$ and the isoelectronic $(\pi\text{-}C_5H_5)_2Fe$, although experiments in which ^{57}Co-labeled cobalticinium tetraphenylborate has been used as a source in conjunction with a narrow single-line absorber have been reported.[14]

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Transition Metal Carbonyl Complexes of the (3)-1,2-Dicarbollide Ion

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Complexes of the (3)-1,2-dicarbollide ion, (3)-1,2-$B_9C_2H_{11}^{2-}$, with molybdenum, tungsten, manganese, and rhenium carbonyls have recently been reported.[1,2]

It was reasonable to assume that chromium, iron, cobalt, and nickel carbonyls would also form stable complexes, analogs of the π-cyclopentadienylmetal carbonyls.

Experimental Section

Chromium, iron, and cobalt carbonyls were obtained from Alfa Inorganics, Inc., Beverly, Mass. Chromatographic polyamide was obtained from Brinkmann Instrumens, Westbury, N. Y. Tetrahydrofuran was distilled from lithium aluminum hydride under nitrogen. All reactions and purification procedures were carried out under nitrogen. A Perkin-Elmer 621 grating infrared spectrophotometer was used for recording the infrared spectra of the complexes and the data given were compiled from spectra obtained using Nujol and Fluorolube mulls or suitable solutions. The ^{11}B nmr spectra at 32 Mcps were obtained using a Varian HA-100 spectrometer. Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Inc., Woodside, N. Y.

$[(CH_3)_4N]_2[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Cr(CO)_3$.—A solution of $(CH_3)_3NH[(3)\text{-}1,2\text{-}B_9C_2H_{12}]$ (2.5 g, 13.0 mmol) dissolved in 100 ml of THF was dropped into a stirring suspension of NaH (2.0 g of a 56% dispersion in mineral oil, 46.7 mmol) in 50 ml of THF. The mixture was stirred at the reflux temperature for 3 hr. During the last 0.5 hr, a slow stream of nitrogen was passed over the solution to remove the trimethylamine generated. After cooling to room temperature, the solution was filtered, chromium hexacarbonyl (2.86 g, 13.0 mmol) was added, and the solution was irradiated in Pyrex with a Hanovia uv light for 72 hr under nitrogen.

The reaction mixture was filtered through Celite, the filtrate was evaporated, and the resulting residue was dissolved in 200 ml of water. The yellow solid obtained upon addition of aqueous tetramethylammonium chloride was collected under nitrogen, washed with water, dissolved in acetone, and chromatographed on polyamide. The bright yellow fraction obtained was recrystallized from acetone–ethanol to give bright yellow crystals of $[(CH_3)_4N]_2[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Cr(CO)_3$ (2.48 g, 45.8%).

Anal. Calcd for $B_9C_{13}H_{35}CrN_2O_3$: B, 23.35; C, 37.47; H, 8.47; Cr, 12.48; N, 6.72. Found: B, 23.34; C, 37.23; H, 8.56; Cr, 12.20; N, 6.65.

The infrared spectrum of the complex shows carbonyl bands at 1875 (s), 1753 (s), and 1728 (s) cm^{-1} (Nujol mull). Other bands in the spectrum occur at 3034 (m), 2960 (w), 2545 (s), 2467 (s), 1482 (s), 1417 (m), 1287 (m), 1169 (w), 1151 (w), 1097 (m), 1068 (w), 1049 (w), 1033 (m), 1016 (m), 986 (m), 949 (s), 883 (w), 853 (w), 770 (w), 740 (w), 714 (w), and 696 (m) cm^{-1}.

The ^{11}B nmr spectrum of the complex in acetonitrile shows resonances at +25.4 ppm (doublet) and +14.7 ppm (doublet) relative to $BF_3 \cdot O(C_2H_5)_2$ with relative intensities 1:2.

$[(CH_3)_4N]_2[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe_2(CO)_4$.—Iron pentacarbonyl (6.9 g, 35.2 mmol) was added to the dicarbollide ion solution obtained from $(CH_3)_3NH[(3)\text{-}1,2\text{-}B_9C_2H_{12}]$ (5.0 g, 26.0 mmol) and NaH (3.0 g of a 56% dispersion in mineral oil, 70.0 mmol) in 200 ml of THF following the procedure described above. The solution was stirred at the reflux temperature for 20 hr and filtered through Celite, and the solvent was removed *in vacuo* (condensation in a trap cooled with acetone–Dry Ice). The residue was dissolved in 200 ml of water and aqueous tetramethylammonium chloride was added. The pink precipitate was washed with water and ethanol and recrystallized from acetone–ethanol to give dark red microcrystalline $[(CH_3)_4N]_2[(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe_2(CO)_4$ (3.41 g, 41.2% yield based upon the boron compound used).

Anal. Calcd for $B_{18}C_{16}H_{46}Fe_2N_2O_4$: B, 30.56; C, 30.18; H,

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7.28; Fe, 17.54; N, 4.40. Found: B, 30.25; C, 30.26; H, 7.34; Fe, 17.99; N, 4.30.

The infrared spectrum of the complex shows carbonyl bands at 1959 (s), 1919 (m), and 1738 (s) cm^{-1} (Nujol mull). Other bands in the spectrum occur at 3034 (m), 2953 (w), 2563 (s), 2523 (s), 1483 (s), 1415 (m), 1288 (w), 1220 (w), 1168 (w), 1150 (w), 1100 (w), 1066 (w), 1028 (m), 993 (m), 918 (w), 874 (w), 863 (w), 747 (w), and 720 (w) cm^{-1}.

The ^{11}B nmr spectrum of the complex in acetone solution shows resonances at +20.9 ppm (doublet), +9.3 ppm (doublet), and −0.1 ppm (doublet) relative to $BF_3 \cdot O(C_2H_5)_2$ with relative intensities approximately 3:5:1.

$[(CH_3)_4N][\pi$-(3)-1,2-$B_9C_2H_{11}]Co(CO)_2$.—Dicobalt octacarbonyl (4.8 g, 14.0 mmol) was added to the dicarbollide ion solution obtained from $(CH_3)_3NH[(3)$-1,2-$B_9C_2H_{12}]$ (15.0 g, 26.0 mmol) and NaH (3.0 g of 56% dispersion in mineral oil, 70.0 mmol) in 200 ml of THF following the procedure described above. The solution was stirred for 1 hr at reflux temperature and filtered through Celite, and the solvent was removed *in vacuo*. The residue was dissolved in 200 ml of water and aqueous tetramethylammonium chloride was added. The green precipitate obtained was washed with water, dissolved in acetone, and chromatographed on polyamide. Recrystallization from ethanol gave yellow crystals of $[(CH_3)_4N][\pi$-(3)-1,2-$B_9C_2H_{11}]Co(CO)_2$ (1.47 g, 17.6% yield based on the boron compound used).

Anal. Calcd for $B_9C_8H_{23}CoNO_2$: B, 30.26; C, 29.89; H, 7.21; Co, 18.33; N, 4.36. Found: B, 30.52; C, 29.06; H, 7.43; Co, 17.38; N, 4.37.

The infrared spectrum of the complex shows carbonyl bands at 2010 (s), 1949 (s), and 1924 (s) cm^{-1} (Nujol mull). Other bands in the spectrum occur at 3026 (m), 2583 (s), 2504 (s), 1480 (m), 1415 (m), 1285 (m), 1201 (w), 1169 (w), 1134 (w), 1110 (m), 1092 (w), 1066 (w), 1020 (m), 987 (m), 948 (s), 883 (w), 868 (w), 771 (w), 737 (w), and 720 (w) cm^{-1}.

The ^{11}B nmr spectrum of the complex in acetonitrile shows resonances at +24.1 ppm (doublet) and +11.6 ppm (doublet) relative to $BF_3 \cdot O(C_2H_5)_2$ with relative intensities approximately 1:2.

Results and Discussion

Chromium hexacarbonyl reacted with a solution of (3)-1,2-dicarbollide ion in tetrahydrofuran under uv irradiation over a prolonged period as in the cases of tungsten and molybdenum carbonyls.[2] Carbon monoxide was given off very slowly and a yellow solution was formed. Although carbon monoxide evolution was not quantitative, the general over-all reaction is in agreement with the equation

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + Cr(CO)_6 \longrightarrow [\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Cr(CO)_3^{2-} + 3CO$$

The tetramethylammonium salt obtained by precipitation of the complex ion from aqueous solution with tetramethylammonium chloride, chromatography on chromatographic polyamide, and recrystallization from acetone–ethanol forms bright yellow microcrystals of $[(CH_3)_4N]_2[\pi$-(3)-1,2-$B_9C_2H_{11}]Cr(CO)_3$, which is insoluble in most organic solvents. The complex is very air sensitive both as a solid and in solution, although decomposition in the solid state is considerably slower. A controlled oxidation of the complex which was expected to yield a dimeric species analogous to the π-cyclopentadienylchromium tricarbonyl dimer[3] was unsuccessful.

The π-(3)-1,2-dicarbollylchromium(0) tricarbonyl ion shows three strong carbonyl bands in the infrared spectrum at 1875, 1753, and 1728 cm^{-1} indicating the presence of three terminal carbonyl groups. The complex exhibits a pattern in the region of 1200–900 cm^{-1} that was found to be characteristic for the (3)-1,2-dicarbollyl group in π complexes with transition metals.[2] The ^{11}B nmr spectra in acetonitrile are poorly resolved but indicate the presence of nine BH groups.

An excess of iron pentacarbonyl when treated with the (3)-1,2-dicarbollide ion in tetrahydrofuran at the reflux temperature for approximately 20 hr gives a dark red solution while giving off carbon monoxide. Dark red microcrystalline $[(CH_3)_4N]_2[\pi$-(3)-1,2-$B_9C_2H_{11}]_2Fe_2(CO)_4$ was obtained from the crude tetramethylammonium salt. The complex in the solid state is only slowly decomposed by air. Solutions in acetone or acetonitrile rapidly decompose in the presence of air.

The (3)-1,2-dicarbollyliron carbonyl complex (as Nujol mull) shows two carbonyl bands in the region of terminal CO groups at 1959 (s) and 1919 (m) cm^{-1} and one in the region of bridging CO groups at 1738 (s) cm^{-1} [1970 (s), 1927 (w), and 1753 (s) cm^{-1} in acetonitrile solution]. The observed diamagnetism of the complex, as in the case of the π-cyclopentadienyliron dicarbonyl dimer, suggests a dimeric structure with an iron–iron interaction, which is in agreement with the observed infrared spectrum in the carbonyl region. This poses an interesting problem. As in the case of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, three structures are possible,[4] *i.e.*, a *cis* isomer in which both dicarbollyl groups lie on one side of an $Fe(CO)_2Fe$ bridge-bonded plane; while the equivalent terminal CO groups lie on the opposite side of the plane; the centrosymmetric *trans* configuration (Figure 1) in which the dicarbollyl groups lie on opposite sides of the bridge-bonded plane; and a metal–metal-bonded species with terminal CO groups only. While it is well agreed[4] that $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ is *trans*-bridge-bonded in the crystalline state, all three isomeric forms undoubtedly[4b] are present in solution in varying amounts, with the ratio of constituents determined by the choice of solvent. In the case of $[(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe_2(CO)_4^{2-}$, the presence of a weak band at 1927 cm^{-1} (acetonitrile solvent) suggests[4] that the dicarbollyl analog is principally a *trans*-bridge-bonded dimer in this solvent system. This is probably due to the higher formal charge of the dicarbollide ligand which should make a *cis* configuration more unstable as compared to the *trans* configuration. An X-ray diffraction study is under way.

The ^{11}B nmr spectrum determined at 32 Mcps in acetone solution exhibited a group of three doublets in a ratio of 3:5:1.

The (3)-1,2-dicarbollyliron carbonyl complex was reduced in aprotic solvents with sodium amalgam to give a yellow solution whose infrared spectrum shows only two carbonyl bands at 1950 and 1890 cm^{-1} and

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[3] T. S. Piper and G. W. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[4] (a) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967); (b) A. R. Manning, *J. Chem. Soc.*, 1319 (1968).

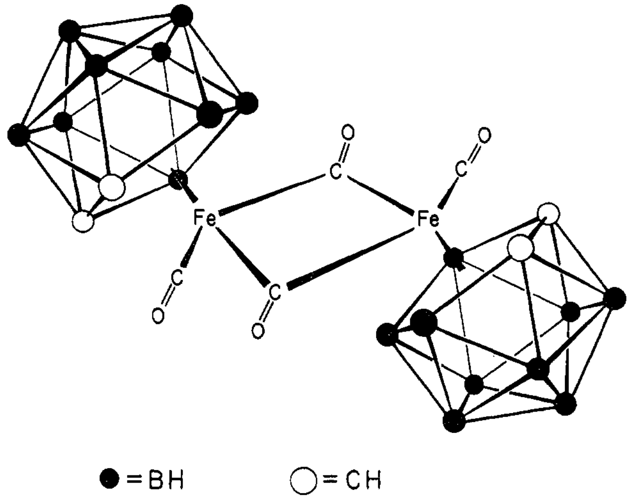

Figure 1.—Schematic structure proposed for the *trans*-[(3)-1,2-$B_9C_2H_{11}]_2Fe_2(CO)_4^{2-}$ ion.

suggests a species containing only terminal carbonyl groups, possibly the [π-(3)-1,2-$B_9C_2H_{11}$]$Fe(CO)_2^{2-}$ ion. No attempts were made to isolate the latter mononuclear ion.

If iron pentacarbonyl and (3)-1,2-$B_9C_2H_{11}^{2-}$ are used in a molecular ratio of 1:1, [π-(3)-1,2-$B_9C_2H_{11}]_2Fe^{2-}$ is formed in addition to the carbonyl complex.

Dicobalt octacarbonyl treated for 1 hr with a tetrahydrofuran solution of the (3)-1,2-dicarbollide ion at the reflux temperature gives a green solution. Precipitation with tetramethylammonium chloride, chromatography on polyamide, and recrystallization from ethanol gives yellow crystals of [$(CH_3)_4N$][π-(3)-1,2-$B_9C_2H_{11}$]$Co(CO)_2$. In both the solid state and solution the complex exhibits extreme air sensitivity, which makes purification very difficult. Even when kept under nitrogen, the solid complex partially decomposes within days.

The complex (Nujol mull) exhibits three strong carbonyl bands in the infrared spectrum at 2010, 1949, and 1924 cm^{-1}. In ethanol solution only the first two bands appear, which is more in agreement with two carbonyl groups. The pattern in the region of 1200–900 cm^{-1} indicates the presence of the (3)-1,2-$B_9C_2H_{11}$ group. The ^{11}B nmr spectrum again shows two doublets with a relative intensity of approximately 1:2 and resembles that of the chromium carbonyl complex.

So far, similar reactions with nickel tetracarbonyl were unsuccessful, owing to purification problems. Although a brown tetramethylammonium salt of an ion displaying both B–H (2520 cm^{-1}) and CO bands (1870 and 1820 cm^{-1}) in the infrared spectrum has been isolated, analytical data and ^{11}B nmr spectra indicate the presence of impurities.

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Sodium 6-Niobo(ethylenediamine)cobaltate(III) and Its Chromate(III) Analog

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In the course of investigating some transition metal heteropolyniobates,[1] compounds of chromium(III) and cobalt(III) with ethylenediamine (en) have been obtained. To our knowledge, these are the first heteropoly complexes reported in which a polydentate ligand, as well as a heavy oxometalate group, is bound to the heteroion.

Experimental Section

Starting Materials.—All materials used were commercially available reagents. Niobium(V) oxide (99.9+%) was obtained through Gallard-Schlesinger Chemical Mfg. Co.

Potassium 6-Niobate.—Niobium(V) oxide was fused with excess KOH in a nickel crucible, and the product was extracted with a minimum amount of water to remove most of the excess KOH. After the crude niobate was washed with an ethanol–water mixture, it was dissolved in water, and the solution was heated and filtered and made about 1 *M* in niobium. The product was precipitated with ethanol,[2] filtered, and washed successively with 1:1 v/v ethanol–water, 95% ethanol, and diethyl ether, and then air dried.

Anal. Calcd for $K_7HNb_6O_{19} \cdot 13H_2O$: Nb, 40.7; H_2O, 17.1. Found: Nb, 40.2; H_2O, 17.5.

Sodium 6-Niobate.—An aqueous solution of potassium 6-niobate, about 1 *M* in niobium, was heated, and sodium acetate was added to an excess concentration of 0.3 *M*. After cooling to 0–5°, the precipitated product was redissolved in a minimum amount of boiling water, and sodium acetate was added to a concentration of 0.3 *M*. After recooling to 0–5°, the recrystallized product was filtered, washed successively with 1:4 v/v ethanol–water, 95% ethanol, and ether, and air dried.

Anal. Calcd for $Na_7HNb_6O_{19} \cdot 15H_2O$: Nb, 43.1; H_2O, 20.8; Na, 12.4. Found: Nb, 42.6; H_2O, 21.6; Na, 11.9.

Tris(ethylenediamine)chromium(III) Iodide Hydrate and *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride.—These were prepared according to published procedures.[3,4] Analyses were satisfactory.

Sodium 6-Niobo(ethylenediamine)cobaltate(III) Hydrate.[5]—A solution of sodium 6-niobate (2.6 g, 12 mg-atoms of Nb) in 60 ml of boiling water was treated with a fresh solution of 0.57 g (2 mmol) of *trans*-[$Co(en)_2Cl_2$]Cl in 20 ml of water. The resultant rose-purple mixture was boiled down to about half its initial volume, and 6 ml of 1 *M* NaOH was added. On continued boiling, the reddish purple solution turned blue-gray and then dark bluish green. The solution was centrifuged to remove a little light-colored fine precipitate. On cooling, a dusty greenish blue solid separated, leaving a red solution. This solid was recrystallized four times from hot 0.2 *M* sodium acetate. The product was finally collected, washed with 1:4 v/v ethanol–water followed by 95% ethanol, and air dried. The yield of greenish tinged blue powder was 0.7 g, about 25%.

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[2] G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd ed, Academic Press, New York, N. Y., 1965, pp 1705, 1706.

[3] J. C. Bailar, Jr., and C. L. Rollinson, *Inorg. Syn.*, **2**, 199 (1946).

[4] J. C. Bailar, Jr., *ibid.*, **2**, 222 (1946).

[5] Nomenclature follows that for heteropolymolybdates and -tungstates. The prefix "niobo" is used similarly to the prefixes "molybdo" and "tungsto."