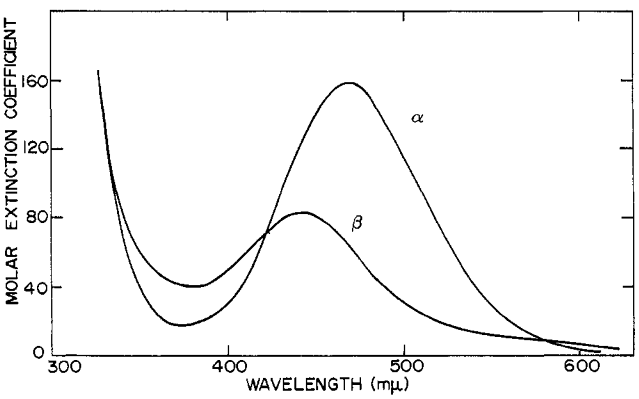

Figure 2.—The electronic spectra of α-[Ni(CRH)](ClO$_4$)$_2$ and β-[Ni(CRH)](ClO$_4$)$_2$ in acetone at room temperature.

secondary amine nitrogens[4] and (2) that the α isomer is substantially more stable than the β isomer. These considerations lead to the assignments of structure I to the α isomer and structure II to the β isomer. This assignment is consistent with the theoretical expectation that form II is more stable than form III when the *meso*-CRH is coordinated in the planar fashion. The readiness with which the β isomer (III) forms the oxalato *cis* complex, in which CRH is folded, is consistent with the structural assignments. Structure III (the β isomer) can be folded into the most stable *cis* form without the inversion of any of the nitrogen atoms. To effect the same transformation the α isomer (II) must undergo inversion of that nitrogen atom in the position *trans* to pyridine. This is a slow process in neutral aqueous media. Therefore, this reaction requires heating in order to proceed in reasonable time. The role of the basicity of sodium oxalate in the formation of the oxalato complex when this must be accompanied by the inversion of nitrogen configuration has been discussed earlier.[2] The configurational relationships are summarized in Figure 3.

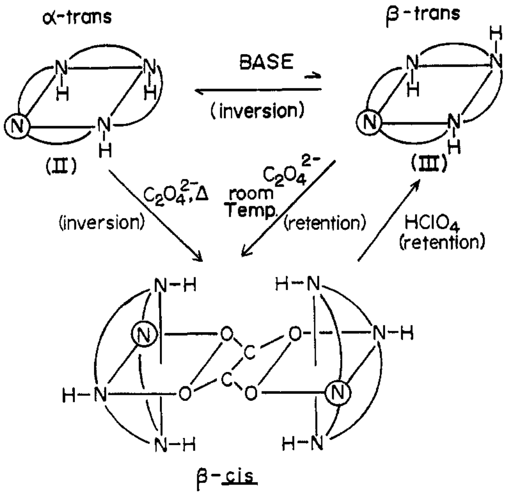

Figure 3.—The stereochemistry of [Ni(CRH)] complexes.

Experimental Section

Preparation of α-[Ni(CRH)](ClO$_4$)$_2$.—This compound was prepared by hydrogenation of [Ni(CR)](ClO$_4$)$_2$ according to the method of Karn.[3] In the process (H_2 over platinum oxide catalyst), a minor product [Ni(*rac*-CRH)](ClO$_4$)$_2$ was also formed, but only the major isomer [Ni(*meso*-CRH)](ClO$_4$)$_2$ is discussed in the text and hereafter in this report. The crude product was recrystallized from hot water. In recrystallization, care should be taken not to heat for a prolonged period in air because it has been observed that the coordinated CRH ligand is oxidized to form a new ligand with one C=N bond under these conditions. The product was isolated as red needles or plate crystals. *Anal.* Calcd: C, 34.62; H, 5.04; N, 10.77. Found: C, 34.41; H, 5.10; N, 10.80. Molar conductivity (in H_2O): 221 mho cm^2/mol (2:1 electrolyte).

Preparation of β-*cis*-[{Ni(CRH)}$_2$C$_2$O$_4$](ClO$_4$)$_2$.—This compound was also prepared by the method of Karn.[3] It exists as violet crystals. *Anal.* Calcd: C, 41.36; H, 5.64; N, 12.06. Found: C, 41.42; H, 5.83; N, 11.82.

Preparation of β-[Ni(CRH)](ClO$_4$)$_2$.—The violet oxalato complex (1.0 g) was suspended and shaken in 30 ml of perchloric acid solution (2:1 concentrated $HClO_4$–H_2O). In a few minutes, yellow crystals separated from the slurry and the shaking was continued until all of the violet material disappeared. The yellow crystals were collected on a filter funnel, washed with water and ethanol, and air dried. *Anal.* Calcd: C, 34.62; H, 5.04; N, 10.77. Found: C, 34.88; H, 5.10; N, 10.98. Molar conductivity (in H_2O): 212 mho cm^2/mol (2:1 electrolyte).

Acknowledgment.—This program has received financial support from the National Science Foundation.

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[4] J. Halpern, A. M. Sargeson, and K. P. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966); D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967); L. G. Warner, N. J. Rose, and D. H. Busch, *ibid.*, **89**, 703 (1967).

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Observations on Reactions of (π-C$_5$H$_5$)Co(π-B$_7$C$_2$H$_9$) Isomers with Electrophiles

BY BRUCE M. GRAYBILL AND M. FREDERICK HAWTHORNE

Received February 19, 1969

Several substitution reactions were attempted on the newly discovered "π-sandwich" cobalt(III) complex containing the $C_5H_5^-$ and $B_7C_2H_9^{2-}$ anions, (π-C$_5$H$_5$)Co(π-1,6-B$_7$C$_2$H$_9$) (I).[1] It was the intent of this study to investigate substitution reactions similar to those which were successful with ferrocene and other metallocenes and to see if the carborane cage or the cyclopentadiene ring of compound I is more reactive with electrophiles.

Acetylation

Friedel–Crafts acylation of compound I with acetyl chloride and aluminum chloride in methylene chloride solvent produced an acetyl derivative, (C$_5$H$_5$)Co(B$_7$C$_2$H$_8$COCH$_3$) (II). The infrared spectrum of the red compound II contained a sharp carbonyl absorption band at 1630 cm^{-1}.

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[1] M. F. Hawthorne and T. A. George, *J. Am. Chem. Soc.*, **89**, 7114 (1967).

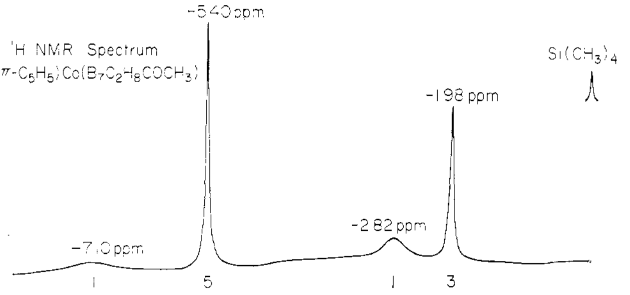

Figure 1.—The 60-Mcps ^{1}H nmr spectrum of acetylated (π-C_5H_5)Co(π-1,6-$B_7C_2H_9$) in $(CD_3)_2CO$.

The nmr spectra of II were very revealing with respect to the position of attack by the acetyl group. The 60-Mcps ^{1}H nmr spectrum of II in deuterioacetone (Figure 1) contained a sharp cyclopentadienyl resonance at τ 4.60 and a methyl proton peak at τ 8.02. Broad absorptions of the two carborane protons appeared at τ 2.9 and 7.2. The 32-Mcps ^{11}B nmr of I and II were essentially the same except for the collapse of one doublet found in the spectrum of I into a singlet centered at +1.1 ppm (relative to $BF_3 \cdot (C_2H_5)_2O$) in the spectrum of II. Figure 2 presents the ^{11}B nmr spectrum of II in deuterioacetone.

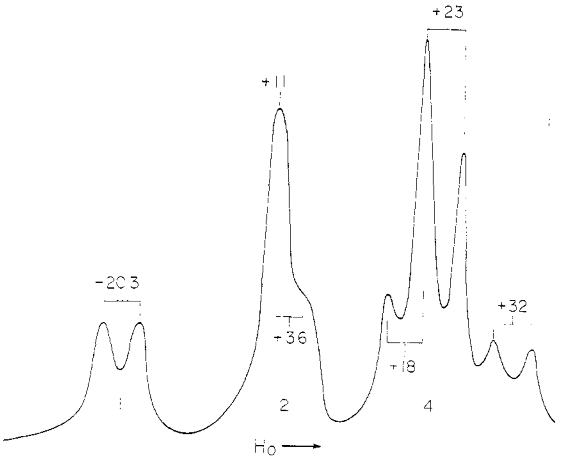

Figure 2.—The 32-Mcps ^{11}B nmr spectrum of acetylated (π-C_5H_5)Co(π-1,6-$B_7C_2H_9$) in acetone.

The fact that no splitting was observed in the 60-Mcps cyclopentadienyl ^{1}H nmr spectrum of II and that a doublet in the 32-Mcps ^{11}B nmr spectrum of the starting material had changed to a singlet proved that the acetyl group was attached to a boron atom of the carborane cage rather than to a carbon of the π-cyclopentadienyl ring. A tentative structural assignment suggests that the acetyl group is probably attached to the number eight boron atom away from the bonding face (Figure 3). This boron atom is the furthest removed from the two carborane carbons and presumably has a high electron density relative to the other boron atoms of the $B_7C_2H_9^{2-}$ ligand.

It is interesting to note that although ferrocene acylates readily on the cyclopentadienyl ring under the same conditions,[2] no acylation on C_5H_5 takes place with I. Even when 2 mol of acetyl chloride–aluminum chloride was used per mole of I, only the boron-substituted derivative II was obtained.

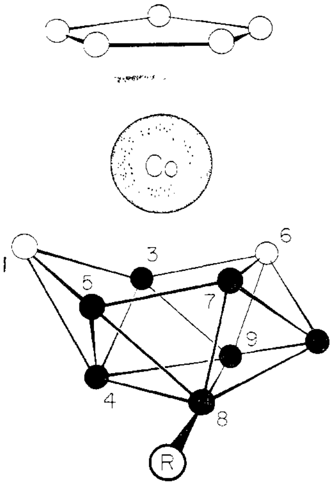

Figure 3.—Proposed structure for the acetyl derivative of (π-C_5H_5)Co(π-1,6-$B_7C_2H_9$) with H atoms removed: ○ O, CH; ●, BH; Ⓡ, $-COCH_3$.

Compound II readily formed an orange 2,4-dinitrophenylhydrazone derivative which exploded violently at 183°. The acetyl derivative dissolved in concentrated hydrochloric acid, as evidenced by the red solution, whereas compound I was insoluble in water or acid. This observation suggests that the acetyl group oxygen atom may be rather easily protonated in aqueous media.

An attempt was made to rearrange compound II from the 1,6- to the 1,10-carborane structure similar to the reported rearrangement of I.[3] At 250° compound II did change from red to yellow, but much decomposition occurred and the acetyl group was completely removed. The facile removal of the acetyl group was also evidenced by an attempted reduction of the carbonyl group of II with $LiAlH_4$. No carbinol was formed, and only extensive decomposition material along with a small amount of I was produced.

The yellow, rearranged isomer[3] of I, (π-C_5H_5)Co(π-1,10-$B_7C_2H_9$), was also subjected to the acylation reaction under the same conditions which yielded II. No acetyl derivative was produced. This may be due to the more symmetrical structure of the rearranged 1,10-$B_7C_2H_9$ cage and the subsequent more equal distribution of ground-state charge on the boron atoms since each boron atom of the 1,10-$B_7C_2H_9$ cage is a near neighbor of an electropositive carbon atom.

Bromination

Bromination of I with excess bromine in carbon tetrachloride solvent at room temperature produced as the main product a dibromo derivative (III) which also contained a small amount of a tribromo product as evidenced by mass spectral analysis. Again the ^{1}H and

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[2] R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458(1952).

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

^{11}B nmr spectra indicated that bromination had taken place on boron of the carborane cage rather than carbon of the π-cyclopentadienyl ring. The C_5H_5 proton resonance for III was a single peak at τ 5.53 (benzene solvent).

The 32-Mcps ^{11}B nmr spectrum of III could not be clearly interpreted owing to extensive overlap of the resonances. A reasonable structure for III could possibly have bromine substituted at the 8 and 10 boron positions of the $B_7C_2H_9$ cage. Single-crystal X-ray diffraction studies are in progress.

Nitration

Compound I was nitrated very easily by stirring a solution of I in methylene chloride over concentrated nitric acid. The infrared spectrum of the semisolid crude product contained strong bands around 1600 and 1300 cm^{-1} which are characteristic of a nitro group. The material was *extremely* shock sensitive and therefore no further work on isolation of a pure product was done.

Experimental Section

Preparation of $(\pi\text{-}C_5H_5)Co(\pi\text{-}1,6\text{-}B_7C_2H_8\text{-}8\text{-}COCH_3)$.—Aluminum chloride, 0.67 g (5 mmol), and acetyl chloride, 0.4 g (5 mmol), were dissolved in 25 ml of dry dichloromethane and placed in a 100-ml, three-necked flask equipped with an addition funnel, a magnetic stirrer, and a condenser with a nitrogen inlet. The flask and contents were cooled to 0° and flushed with dry nitrogen. To the cooled mixture was added a solution of 1 g (4.3 mmol) of $(C_5H_5)Co(B_7C_2H_9)$ (I) in 25 ml of dichloromethane. The mixture was stirred for 45 min at 0°, then warmed to room temperature, and finally refluxed for 3 hr.

The reaction solution was then poured into ice water and the layers were separated. The water layer was extracted once with CH_2Cl_2. The combined dichloromethane extract was dried over magnesium sulfate, filtered, and evaporated to dryness. The product may be recrystallized from ether–hexane or chromatographed with a silica gel column. The red acetyl derivative was eluted with 1:1 C_6H_{14}–CH_2Cl_2 whereas unreacted starting material came off the column first with 9:1 C_6H_{14}–CH_2Cl_2; total yield, 6.8 g (72%); mp 162°. *Anal.* Calcd for $(C_5H_5)Co(B_7C_2H_8COCH_3)$: C, 39.32; H, 5.87; B, 27.55; Co, 21.44. Found: C, 39.41; H, 5.88; B, 27.42; Co, 21.33. A 2,4-dinitrophenylhydrazone derivative was easily prepared and recrystallized as small orange plates from ethanol. The compound explodes with violence at 183°.

Bromination of $(C_5H_5)Co(B_7C_2H_9)$.—$(C_5H_5)Co(B_7C_2H_9)$ (I), 0.5 g (2.2 mmol), was dissolved in 50 ml of carbon tetrachloride along with 3 ml (8.8 g, 55 mmol) of bromine. The mixture was stirred in a round-bottomed flask at room temperature for 20 hr. Some orange solid crystallized from solution. The reaction mixture was poured into water and the excess bromine was removed by extraction with aqueous sodium sulfite. Some additional methylene chloride was added and the organic layer was washed several times with water. The carbon tetrachloride extract was separated, dried over magnesium sulfate, filtered, and evaporated to dryness. The crude product was chromatographed from a silica gel column. Complete elution was accomplished with hexane–methylene chloride (1:1). After concentration of the column extracts, 0.55 g of orange solid was filtered from the hexane. Two recrystallizations from ether–hexane afforded orange crystals which melted at 129–130° (the orange melt slowly turns yellow at 130–140°). *Anal.* Calcd for $(C_5H_5)Co(B_7C_2H_7Br_2)$: C, 21.53; H, 3.09; B, 19.38; Co, 15.09; Br, 40.92. Found: C, 21.21; H, 3.09; B, 19.83; Co, 16.13; Br, 42.71. (A mass spectrum of the sample indicated that a small amount of a tribromo derivative was also formed.)

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Polyhedral Manganese Carbonyl Derivatives of the $B_6C_2H_8^{2-}$ Ligand

BY A. DENISE GEORGE AND M. FREDERICK HAWTHORNE

Received March 7, 1969

It has been found that 1,3-$B_7C_2H_{11}^{2-}$ reacts with some group VIII transition metal salts to give π complexes containing the dicarbazapide ligand $B_7C_2H_9^{2-}$.[1] It therefore seemed of interest to examine the behavior of $Na_2B_7C_2H_{11}$ with transition metal carbonyl derivatives. The formation of stable complexes in the reaction of the dicarbollide ion with group VII pentacarbonyl halides has already been demonstrated;[2] hence the reactions of $Na_2B_7C_2H_9R_1R_2$ (R_1 and R_2 are substituents at carbon) with group VII carbonyls were selected as an area of study.

Reactions with Manganese Carbonyls.—In all of the reactions involving $Na_2B_7C_2H_9R_1R_2$, a suspension of the salt was prepared in diethyl ether. It has been shown[1] that under the reaction conditions employed, 2 mol of hydrogen is evolved and the $B_7C_2H_{11}^{2-}$ ion is formed.

$$B_7C_2H_{13} + 2NaH \longrightarrow Na_2B_7C_2H_{11} + 2H_2$$

When molar equivalents of manganese pentacarbonyl bromide and $Na_2B_7C_2H_{11}$ were heated in tetrahydrofuran at the reflux temperature, the mixture turned from yellow to deep amber, gas was evolved, and sodium bromide precipitated out. When the reaction was carried out at room temperature, the products were identical with those formed in refluxing tetrahydrofuran, indicating the instability of any assumed intermediate containing five carbonyl groups. Infrared spectra of the tetramethylammonium salt of the isolated product anion contained a B–H stretch at 2490 cm^{-1} and carbonyl stretching bands at 1992 and 1910 cm^{-1} (Table IV). The elemental analysis, formula weight, and equivalent weight (Table I) satisfied, much to our suprise, the general formula $B_6C_2H_8Mn(CO)_3^-$ for the anion. Table II presents the 32-Mcps ^{11}B nmr spectrum of the proposed compound $(CH_3)_4N[B_6C_2H_8Mn(CO)_3]$, which consists of four discrete doublets. If the low-field doublet is assumed to be of relative inten-

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[1] (a) M. F. Hawthorne and T. A. George, *J. Am. Chem. Soc.*, **89**, 7114 (1967); (b) T. A. George and M. F. Hawthorne, *ibid.*, in press.

[2] (a) M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965); (b) 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, *ibid.*, **90**, 879 (1968).