

pounds at 110° or in a few cases at a slightly higher temperature, the water and ammonia are lost. A few of the nickel(II) complexes after drying are diamagnetic which is consistent with a square-planar arrangement of the two bidentate ligands.

The 4-Br and 4-NO₂ chelates of nickel(II) were each prepared by two methods. (Table I shows that after being dried at 110°, they are of the same stoichiometry.) Table IV shows that drying at 110° yields a diamagnetic or paramagnetic complex depending on the method of synthesis. We are investigating this interesting phenomenon which will be the subject of a future publication.

In no case where an electron-rich group in the ortho position is present (F, Cl, etc.) were diamagnetic compounds obtained. The nickel(II) compounds with halide in the 2 position contained little or no water or ammonia of coordination. This is consistent with the steric effect of the ortho substituent reported previously.^{2,3} It is tempting to suggest that these groups occupy the fifth and sixth coordination sites yielding tetragonally distorted octahedral coordination as suggested by Zacharias, *et al.*⁹ However, the ortho-substituent coordination does not explain the anomalous moments for the 2-Br and the 2-I derivatives. Preliminary results show that both compounds obey the Curie-Weiss law from 295 to 120°K. Hence the possibility of the tetragonal field being such that several states can be

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thermally populated, *i.e.*, ¹A ⇌ ³B in *D*_{4h} microsymmetry as found for some nickel complexes,¹⁰ can be eliminated. Likewise the ortho-substituted coordination does not explain the paramagnetic results obtained with the compounds which do not contain an electron-rich group in the 2 position.

It seems probable that with the ortho-substituted derivatives, as well as the others listed in Table IV (after drying), the paramagnetism is due to either tetrahedral structures or pseudooctahedral coordination through intermolecular association in the crystal lattice.¹¹ As the latter seems unlikely with the ortho-substituted complexes, we tentatively suggest that, in the absence of solvent, the compounds listed in Table IV are either tetrahedral or square planar. With the 2-Br and 2-I compounds we suggest that the solid contains both structures.¹²

Electronic spectra are of little help in distinguishing the various structural possibilities because strong charge-transfer bands obscure the d-d bands, which would be of limited value anyway due to the rather low real symmetry of the compounds reported here.

A complete investigation of the temperature dependency of the magnetic susceptibilities reported above is in progress.

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Reactions of Several Cationic Organometallic Isocyanide Complexes with Sodium Borohydride

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Received October 5, 1970

Reactions of borohydride ion with C₅H₅Fe(CO)(CNCH₃)₂⁺, C₅H₅Mo(CO)₂(CNCH₃)₂⁺, and C₅H₄CH₃Mn(NO)(CNCH₃)₂⁺ occur with addition of BH units across the two C≡N bonds in the coordinated isocyanide ligands. With borohydride ion and C₅H₅Fe(CNCH₃)₃⁺ addition of BH units to the three isocyanide ligands occurs. Reaction of C₅H₅Fe(CO)(CHNCH₃)₂BH₂ and C₅H₄CH₃Mn(NO)(CHNCH₃)₂BH₂ with (C₆H₅)₃C⁺BF₄⁻ leads to substitution by fluorine of the two terminal boron hydride protons in these complexes, giving C₅H₅Fe(CO)(CHNCH₃)₂BF₂ and C₅H₄CH₃Mn(NO)(CHNCH₃)₂BF₂, respectively. All products were characterized by analyses, mass spectra, and nmr (¹H and ¹¹B) and infrared spectra.

Reduction of cationic transition metal organometallic complexes with borohydride ion is most often accompanied by hydride transfer to the metal or to one of the ligand groups. The π-hydrocarbon ligands are particularly well known to add hydride ion in these reactions. Among the earliest work in this area is the reduction of the cobalticinium and rhodicinium ions to give the uncharged cyclopentadienylcyclopentadienemetal complexes¹ and the reduction of cycloheptatrienylchromium tricarbonyl cation to cycloheptatrienechromium tricarbonyl.² More recently π-

arene ligands have been shown to add a hydride ion to give cyclohexadienylmetal complexes,^{3,4} and π-olefin-metal complexes have been converted to σ-alkylmetal complexes with borohydride.⁵ Although in the initial cobalticinium and rhodicinium work¹ it was suggested that the hydride ion became attached to the ring in the endo position, there now seems to be ample evidence, including finally an X-ray crystallographic study,⁶ that this is incorrect; substitution occurs in the exo position only. The same stereochemistry is

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TABLE I
INFRARED SPECTRAL DATA (CM⁻¹)

Compound	ν_{CO}	ν_{NO}	$\nu_{\text{C=N}}$	Other
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CHNCH}_3)_2\text{BH}_2^b$	1950 s	...	1555 s	2930 mw, 2300 w, 1405 w, 1350 m, 1155 w, 1005 w, 870 vw, 815 w, 590 w, 550 m
$\text{C}_5\text{H}_5\text{Fe}(\text{CHNCH}_3)_3\text{BH}^a$	1525 s	2420 m, 2380 w, 1480 s, 1410 s, 1330 s, 1140 m, 1105 w, 1070 w, 1000 m, 810 m, 800 m, 750 w, 695 m, 490 m
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{CHNCH}_3)_2\text{BH}_2^b$	1955 s, 1865 s	...	1565 s	3250 m, 3000 w, 2950 m, 2370 m, 2330 m, 1455 m, 1435 m, 1405 m, 1340 s, 1180 w, 1140 s, 1005 m, 960 w, 880 w, 800 m, 600 w, 570 m, 530 s, 510 m, 470 m
$\text{C}_5\text{H}_4\text{CH}_3\text{Mn}(\text{NO})(\text{CHNCH}_3)_2\text{BH}_2^a$...	1687 s	1549 m, 1523 w	2910 w, 2388 w, 1342 m, 1193 w, 1147 w, 1040 w, 820 w
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CHNCH}_3)_2\text{BF}_2^a$	1965 s	...	1545 s	3120 mw, 1440 m, 1420 s, 1355 s, 1150 m, 1110 m, 1065 s, 1035 s, 1020 s, 940 w, 930 w, 910 w, 850 m, 840 m, 760 w, 650 w, 590 m, 550 s
$\text{C}_5\text{H}_4\text{CH}_3\text{Mn}(\text{NO})(\text{CHNCH}_3)_2\text{BF}_2^a$...	1700 s	1551 m, 1520 w	2950 w, 1455 w, 1415 w, 1350 w, 1143 w, 1105 w, 1020 m, 915 w, 883 w, 822 w, 720 w
$\text{C}_5\text{H}_4\text{CH}_3\text{Mn}(\text{NO})(\text{CNCH}_3)_2^+\text{PF}_6^-^a$...	1873 s	2219 s ($\nu_{\text{C=N}}$)	3120 w, 1480 w, 1447 w, 1410 m, 1383 m, 830 s (ν_{PF})

^a Nujol or Fluorolube mulls. ^b CHCl_3 solutions, KBr cells.

TABLE II

¹H AND ¹¹B NMR DATA

Compound	Proton spectra, ^a chem shift, τ (intens)	¹¹ B spectra, ^b δ (J_{BH} or J_{BF})
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CHNCH}_3)_2\text{BH}_2^c$	C_5H_5 , 5.2 (5); CH_3 , 6.7 (6); CH , -1.1 (2)	+5.9 (96 Hz, triplet)
$\text{C}_5\text{H}_5\text{Fe}(\text{CHNCH}_3)_3\text{BH}^c$	C_5H_5 , 5.2 (5); CH_3 , 6.7 (9); CH , -2.0 (3)	+2.6 (107 Hz, doublet)
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{CHNCH}_3)_2\text{BH}_2^c$	C_5H_5 , 4.4 (5); CH_3 , 6.60 (6); CH , -1.3 (2)	...
$\text{C}_5\text{H}_4\text{CH}_3\text{Mn}(\text{NO})(\text{CHNCH}_3)_2\text{BH}_2^c$	$\text{C}_5\text{H}_4\text{CH}_3$, 5.13 (4) (split), 8.08 (3); CH_3 , 6.60 (6); CH , -0.91 (2)	+2.9 (68 Hz, triplet)
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CHNCH}_3)_2\text{BF}_2^c$	C_5H_5 , 5.2 (5); CH_3 , 6.6 (6); CH , -1.7 (2)	-0.7 (31 Hz, triplet)
$\text{C}_5\text{H}_4\text{CH}_3\text{Mn}(\text{NO})(\text{CHNCH}_3)_2\text{BF}_2^c$	$\text{C}_5\text{H}_4\text{CH}_3$, 5.16 (4) (split), 8.18 (3); CH_3 , 6.67 (6); CH , -1.2 (2)	-1.6 (33 Hz, triplet)
$\text{C}_5\text{H}_4\text{CH}_3\text{Mn}(\text{NO})(\text{CNCH}_3)_2^+\text{PF}_6^-^d$	$\text{C}_5\text{H}_4\text{CH}_3$, 5.12 (4), 8.58 (3); CH_3 , 6.85 (6)	...

^a TMS internal standard; all peaks singlets except as noted. ^b $\text{Vs. BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ external standard. ^c CDCl_3 solution. ^d Acetone-*d*₆.

seen in reactions of cationic complexes with alkyl- and aryllithium reagents.⁷

Three other types of reactions have been observed in borohydride reactions with cationic organometallic complexes, though there exist only very limited examples of each. In 1961, Davison, Green, and Wilkinson reported reactions of borohydride ion with $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3^+$ to give $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$,⁸ a reaction proceeding with displacement of carbonyl by hydride. A similar reaction is observed with $\text{C}_5\text{H}_5\text{M}(\text{CO})_4^+$ ($\text{M} = \text{Mo}, \text{W}$).⁷ Several reductions to dinuclear species, including the reduction of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}^+$ and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Co}(\text{CO})_3^+$ to $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})\text{NO}]_2^9$ and $[(\text{C}_6\text{H}_5)_3\text{PCo}(\text{CO})_3]_2$,¹⁰ respectively, are known. It is possible to postulate their formation by way of an unstable metal-hydride intermediate. Still more recently, the interesting reduction of a coordinated carbonyl ligand to a σ -methyl group was observed in our group.⁷

Observed in borohydride reductions of uncharged organometallic halides such as $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ is another type of reaction product, in which the borohydride unit is linked to the metal through one or more hydrogen bridging units.¹¹

We have been involved in extensive studies on cat-

ionic metal isocyanides and in the course of our work have run borohydride reactions with a number of these species. In contrast to the observations with analogous carbonyl complexes, a general reaction involving incorporation of the BH_4 into the complex was found to occur. In this reaction we postulate BH addition to the carbon-nitrogen multiple bond of two or three cis isocyanides.¹² The full study of preparation and characterization of these complexes is reported in this paper.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Molecular weights were obtained from the mass spectra, run on an AEI MS-902. Infrared spectra were recorded on a Beckman Model IR-10 double-beam grating spectrophotometer. The ¹H nmr were recorded on Varian A-60 and T-60 spectrometers. The ¹¹B nmr were recorded on a Varian HA-100 spectrometer, at 32.1 MHz. These data are given in Tables I and II.

Chromatographic separations were made on Fisher aluminum oxide. Tetrahydrofuran was dried by distillation from lithium aluminum hydride. Acetonitrile was dried by refluxing over calcium hydride, distillation onto P_4O_{10} , and distillation from P_4O_{10} onto molecular sieves. These solvents were deaerated by purging with nitrogen as a further precaution. The preparation and handling of methyl isocyanide (*caution!* toxic) is described in ref 13. The complexes $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNCH}_3)_2^+\text{PF}_6^-$ and $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{CNCH}_3)_2^+\text{PF}_6^-$ were obtained by metathetical

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reactions in aqueous solution from the iodide salts which have been reported previously by Coffey,¹⁴ and the complex $C_5H_5Fe(CNCH_3)_3^+PF_6^-$ was obtained in like manner from the known chloride salt.¹⁵ These PF_6^- salts were easily crystallized from acetone-water. The complex $C_5H_5Mn(NO)(CO)_2^+PF_6^-$ was prepared by the method of King.¹⁶ Other starting materials were commercial samples.

As routine procedure all manipulations were carried out under nitrogen.

Reaction of $C_5H_5Fe(CO)(CNCH_3)_2^+PF_6^-$ with $NaBH_4$.—A mixture of 12 g (32 mmol) of $C_5H_5Fe(CO)(CNCH_3)_2^+PF_6^-$ and 3.6 g (96 mmol) of $NaBH_4$ was stirred at 0° in tetrahydrofuran (50 ml) for 2 hr. A dark yellow-brown solution resulted. The solvent was evaporated and the residue was extracted with benzene. After being reduced in volume, this solution was chromatographed on an alumina column prepared with benzene. Development of the column by elution with benzene produced four bands: one yellow-orange and three red-violet in order of increasing retention time.

Band 1 eluted with benzene to give a yellow solution. Evaporation of solvent gave yellow crystals, $C_5H_5Fe(CO)(CHNCH_3)_2BH_2$ (3.6 g, 50%), mp 123–124°. *Anal.* Calcd for $C_{10}H_{15}ON_2BF_2$: C, 48.75; H, 6.10; N, 11.40; B, 4.47; Fe, 22.78; mol wt 246. Found: C, 49.36; H, 5.90; N, 11.24; B, 4.44; Fe, 22.58; mol wt 246 from mass spectrum.

Band 2 eluted with benzene to give a red solution. Evaporation of solvent gave red-violet crystals identified by an infrared spectrum as $[C_5H_5Fe(CO)]_2$ (trace amounts). The third and fourth bands also gave small amounts of red solids of apparent low stability. The infrared spectra of these complexes suggest that they are $(C_5H_5Fe)_2(CO)_3(CNCH_3)$ and $(C_5H_5Fe)_2(CO)_2(CNCH_3)_2$; analysis later confirmed the identity of the former. Further supporting this contention is the synthesis of these complexes in the direct reaction of $[C_5H_5Fe(CO)]_2$ and methyl isocyanide.¹⁷ We will describe their full characterization at a later time.

Reaction of $C_5H_5Mo(CO)_2(CNCH_3)_2^+PF_6^-$ with $NaBH_4$.—A mixture of 6.0 g (13.5 mmol) of $C_5H_5Mo(CO)_2(CNCH_3)_2^+PF_6^-$ and 1.5 g (40.5 mmol) of $NaBH_4$ was stirred at 0° in 50 ml of tetrahydrofuran for 24 hr, giving a dark yellow-brown solution. Work-up, involving chromatography on alumina, gave yellow crystalline $C_5H_5Mo(CO)_2(CNCH_3)_2BH_2$ (0.8 g, 19%), mp 132–134° dec. *Anal.* Calcd for $C_{11}H_{15}N_2BMoO_2$: C, 42.0; H, 4.78; N, 8.92; B, 3.50; mol wt 314. Found: C, 41.99; H, 4.81; N, 8.53; B, 3.70; mol wt 314 from mass spectrum.

Reaction of $C_5H_5Fe(CNCH_3)_3^+PF_6^-$ with $NaBH_4$.—A mixture of 5.0 g (12.8 mmol) of $C_5H_5Fe(CNCH_3)_3^+PF_6^-$ and 1.4 g (38.6 mmol) of $NaBH_4$ in 50 ml of tetrahydrofuran was stirred at room temperature for 48 hr, giving a dark yellow-brown solution. The work-up, similar to those described above, gave only one isolable compound, $C_5H_5Fe(CHNCH_3)_3BH$, as yellow crystals (0.7 g, 21%), mp 151–155°. *Anal.* Calcd for $C_{11}H_{15}FeN_3B$: C, 51.00; H, 6.95; N, 16.20; B, 4.25; Fe, 21.60; mol wt 259. Found: C, 51.66; H, 7.28; N, 16.11; B, 4.08; Fe, 20.97; mol wt 259 from mass spectrum.

Attempted Reaction of $C_5H_5Fe(CO)_2CNCH_3^+PF_6^-$ and $NaBH_4$.—A sample of $C_5H_5Fe(CO)_2CNCH_3^+PF_6^-$ (6.0 g, 16.5 mmol) and $NaBH_4$ (1.88 g, 49.5 mmol) was stirred in 250 ml of tetrahydrofuran at 0° for 8 hr. The solvent was evaporated, and the residue was dissolved in a minimum of benzene and filtered. The filtrate was chromatographed on alumina; benzene caused three bands to elute. The first band was yellow. On evaporation it yielded 0.16 g of $C_5H_5Fe(CO)(CHNCH_3)BH_2$, 4.0% yield, identified by its infrared spectrum and melting point. The second band (red) was the major one; on evaporation it gave 1.40 g of $[C_5H_5Fe(CO)]_2$, 24% yield, identified by its infrared spectrum. The third band off the column gave 0.28 g of a red solid. This was identified as $(C_5H_5Fe)_2(CO)_3(CNCH_3)$ (4.5% yield).

Preparation of $C_5H_4CH_3Mn(NO)(CNCH_3)_2^+PF_6^-$.—Solid $C_5H_4CH_3Mn(NO)(CO)_2^+PF_6^-$ (15.0 g, 41 mmol) was dissolved in 300 ml of acetone, and to this was added 5.1 g (124 mmol) of methyl isocyanide. Gas evolution occurred immediately. The reaction mixture was refluxed for 2 hr. The resulting deep red solution was filtered and 250 ml (95%) of ethanol was added.

The volume of the solution was reduced by evaporation at water aspirator pressure until a red crystalline solid just began to deposit. Further crystallization was accomplished at –20°. The red crystals were filtered cold and washed with ethyl ether. The yield of $C_5H_4CH_3Mn(NO)(CNCH_3)_2^+PF_6^-$ was 14.3 g (89%). The product could be recrystallized from acetone-ether; mp 159–160°. *Anal.* Calcd for $C_{10}H_{13}N_5OMnPF_6$: C, 30.70; H, 3.35; N, 10.75. Found: C, 30.83; H, 3.43; N, 10.62.

Reaction of $\pi-C_5H_4CH_3Mn(NO)(CNCH_3)_2^+PF_6^-$ with $NaBH_4$.—A 5.0-g (13-mmol) sample of $C_5H_4CH_3Mn(NO)(CNCH_3)_2^+PF_6^-$ was added to 250 ml of tetrahydrofuran at 0°. To this was added 0.80 g (21 mmol) of $NaBH_4$. The suspension was stirred for 0.5 hr at 0° and an additional 1.5 hr at 25°. The solvent was removed from the resulting purple solution. The dark solid was extracted with benzene (25 ml) and chromatographed on alumina using benzene as the eluent. A single purple band eluted. Evaporation of the benzene gave 1.8 g (53%) of a purple crystalline air-stable material, $C_5H_4CH_3Mn(NO)(CHNCH_3)_2BH_2$, mp 108° dec. *Anal.* Calcd for $C_{10}H_{17}N_3OBMn$: C, 46.01; H, 6.57; N, 16.11; mol wt 261. Found: C, 45.60; H, 6.39; N, 15.84; mol wt 261 from mass spectrum.

Reaction of $C_5H_5Fe(CO)(CHNCH_3)_2BH_2$ and $(C_6H_5)_3C^+BF_4^-$.—A mixture of 0.5 g (2 mmol) of $C_5H_5Fe(CO)(CHNCH_3)_2BH_2$ and 0.74 g (2.2 mmol) of $(C_6H_5)_3C^+BF_4^-$ was stirred at room temperature in ~40 ml of anhydrous acetonitrile for 24 hr. The acetonitrile was evaporated and the residue was extracted with hexane. Evaporation of the hexane gave triphenylmethane, as a white crystalline solid. The yellow, hexane-insoluble part of the residue was purified by chromatography on an alumina column prepared with benzene. Elution of the yellow band with benzene gave a yellow solution. Evaporation of the solvent gave yellow crystals, $C_5H_5Fe(CO)(CHNCH_3)_2BF_2$ (0.22 g, 39%), mp 165–167° dec. *Anal.* Calcd for $C_{10}H_{15}N_2F_2BFeO$: C, 42.60; H, 4.61; N, 9.94; Fe, 19.85; mol wt 282. Found: C, 42.85; H, 4.72; N, 9.89; Fe, 19.92; mol wt 282 from mass spectrum.

Reaction of $C_5H_4CH_3Mn(NO)(CHNCH_3)_2BH_2$ and $(C_6H_5)_3C^+BF_4^-$.—A 0.70-g sample (2.7 mmol) of $C_5H_4CH_3Mn(NO)(CHNCH_3)_2BH_2$ was added to 50 ml of dry acetonitrile. To this was added 1.0 g (3.0 mmol) of $(C_6H_5)_3C^+BF_4^-$ and the mixture was stirred at 25° for 3 hr. The reaction mixture was filtered and the solvent was evaporated. The residue was extracted with a 1:1 benzene-chloroform mixture. Chromatography of the resulting purple solution on alumina with benzene gave a light yellow material identified as $(C_6H_5)_3CH$. Further elution with chloroform gave a purple band which upon evaporation of the solvent gave 0.32 g (40%) of air-stable, purple, crystalline $C_5H_4CH_3Mn(NO)(CHNCH_3)_2BF_2$, mp 140° dec. *Anal.* Calcd for $C_{10}H_{13}N_3OMnBF_2$: C, 40.43; H, 5.09; N, 14.16; mol wt 297. Found: C, 40.17; H, 4.89; N, 14.02; mol wt 297 from mass spectrum.

The reaction of $C_5H_5Fe(CHNCH_3)_3BH$ and $(C_6H_5)_3C^+BF_4^-$ under similar conditions gave no reaction and recovery of starting material.

Discussion

The reaction of $C_5H_5Fe(CO)(CNCH_3)_2^+$ and BH_4^- leads primarily to one product, $C_5H_5Fe(CO)(CHNCH_3)_2BH_2$, in good yield. In addition, small amounts of $[C_5H_5Fe(CO)]_2$ and two isocyanide-substituted derivatives of this, $(C_5H_5Fe)_2(CO)_3(CNCH_3)$ ^{17,18} and probably $(C_5H_5Fe)_2(CO)_2(CNCH_3)_2$, were also observed though in small quantities. Cyclopentadienyliron dicarbonyl dimer is known to occur regularly in many reactions of cyclopentadienyliron carbonyls and is not unexpected here; its synthesis suggests a facile carbonyl-isocyanide ligand exchange in the reaction system. The small amounts of isocyanide-substituted dimers may arise from direct reduction of the cationic complex, followed by ligand exchange, or by substitution of $[C_5H_5Fe(CO)]_2$ by small amounts of free isocyanide which no doubt are present in the reaction

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(18) A compound analogous to this was prepared on borohydride reduction of $C_5H_5Fe(CO)(CNC_6H_5)I$; an X-ray crystallographic study of this showed that the isocyanide was found in a bridging position: K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Commun.*, 181 (1965).

system because of decomposition. In any event the relatively small amount of these dinuclear species, which in total yield does not exceed several per cent, is a striking feature of this reaction. It means that the primary pathway of the reaction is not one analogous to that seen in the analogous carbonyl systems involving ligand displacement to give a metal hydride, which would subsequently give dimer formation. The second general reaction type previously observed for hydride reactions is the addition to a π -hydrocarbon group; this reaction appears not to have occurred here either.

It is interesting that the reaction of $C_5H_5Fe(CO)_2(CNCH_3)^+$ and borohydride appears to be a typical reaction; the main products are $[C_5H_5Fe(CO)_2]_2$ and $(C_5H_5Fe)_2(CO)_3(CNCH_3)$, both of which could arise from unstable intermediate hydride formation or from direct reduction. A very small amount of $C_5H_5Fe(CO)(CHNCH_3)_2BH_2$ does arise; its occurrence supports our earlier contention that ligand exchange or substitution is probably occurring in the starting material since the origin of this material is virtually certain to be $C_5H_5Fe(CO)(CNCH_3)_2^+$.

The primary product in the $C_5H_5Fe(CO)(CNCH_3)_2^+$ -borohydride reaction was a yellow crystalline solid, obtained in over 50% yield. It is a covalent substance, being readily soluble in petroleum solvents and subliming *in vacuo* at a low temperature. Its composition was determined by elementary analyses and by its mass spectrum which showed a parent peak at m/e 246, correct for the formulation of a 1:1 adduct of cation and anion, $C_5H_5Fe(CO)(CHNCH_3)_2BH_2$.

That this reaction was a general one was established by the isolation of analogous compounds $C_5H_5Mo(CO)_2(CHNCH_3)_2BH_2$ and $C_5H_4CH_3Mn(NO)(CHNCH_3)_2BH_2$ from reactions of borohydride ion with $C_5H_5Mo(CO)_2(CNCH_3)_2^+$ and $C_5H_4CH_3Mn(NO)(CNCH_3)_2^+$, respectively. Parenthetically we note that the compound $C_5H_4CH_3Mn(NO)(CNCH_3)_2^+$ had not previously been reported. It is easily synthesized in a direct reaction of $C_5H_4CH_3Mn(CO)_2NO^+$ with excess methyl isocyanide in refluxing acetone. Substitution reactions of $C_5H_4CH_3Mn(CO)_2NO^+$ with various ligands (primarily phosphorus donor ligands) have been studied earlier¹⁹⁻²¹ and it has been shown that replacement of both carbonyls is possible.

Infrared and nmr spectra for these three compounds support a tentative structural assignment. In the infrared spectra of all three compounds, ν_{BH} absorptions were noted. The $\nu_{C=N}$ absorption around 2200 cm^{-1} , associated with terminal isocyanide ligands, was lacking, but for each compound a strong new absorption at approximately 1500 cm^{-1} was seen. This absorption was ascribed to $\nu_{C=N}$. The other characteristic absorptions such as ν_{CO} in $C_5H_5Fe(CO)(CHNCH_3)_2BH_2$ and in $C_5H_5Mo(CO)_2(CHNCH_3)_2BH_2$ and ν_{NO} in $C_5H_4CH_3Mn(NO)(CHNCH_3)_2BH_2$ were seen as expected. In the proton nmr spectra, resonances were observed for the protons in the cyclopentadienyl or methylcyclopentadienyl groups. In addition there was a singlet absorption from two equivalent methyl groups (intensity 6) and a very low field resonance at about $\tau -1.0$ (intensity 2). The resonance as-

sociated with the two remaining protons was not observed, but there is compelling evidence that these protons are present in a BH_2 group within the molecule, since absorptions for ν_{BH} are evident in the infrared spectrum and since the ^{11}B spectrum shows the 1:2:1 triplet pattern, expected for coupling to two spin $1/2$ nuclei. Presumably the resonance is broad and of low intensity, so that it could not be observed. It is appropriate to note that in tris(pyrazolylborate) anions,²² and presumably in metal complexes of this ligand,²³ the hydrogen of the BH group is also not observed in the nmr spectra owing to the broadness and multiplicity of this resonance.

Several structures can be proposed for the ligand system in these complexes; three of the most likely alternatives are given in Figure 1. Our preference is

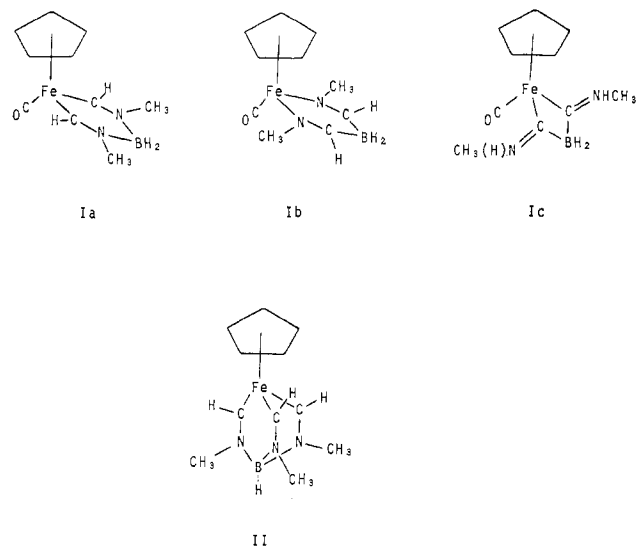
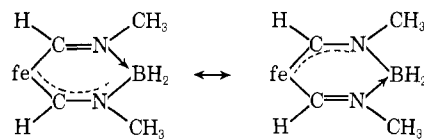


Figure 1.—Possible structures of $C_5H_5Fe(CO)(CHNCH_3)_2BH_2$ and $C_5H_5Fe(CHNCH_3)_2BH$.

strongly in favor of the first of these structures (Ia), but this choice is basically intuitive since the available data could be rationalized for each. The formation of a complex having structure Ia can be envisioned to follow from a straightforward addition of two $B^{\delta+}H^{\delta-}$ units to the multiple $C\equiv N$ bonds in *cis* $C\equiv NCH_3$ groups. The hydridic hydrogen would then end up on the carbon atom of the isocyanide; presumably this atom, like the carbon atom in metal carbonyls,²⁴ bears partial positive character. Nucleophilic attack at both carbonyls⁷ and at isocyanides²⁵ has been observed in the past.

Assuming this structure, we can describe the bonding in terms of two canonical forms of major importance, which involve ligand bonding to the metal by a σ -bonded group and an ylide (carbene) group, *viz.*



where $fe = C_5H_5Fe(CO)$. The localized canonical struc-

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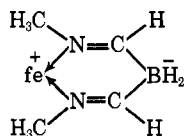
(23) S. Trofimenko, *ibid.*, **91**, 588 (1969).

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ture allows one to see the EAN rule agreement for this compound. A delocalized structure is necessary to be in accord with the nmr equivalence of N-CH₃ and C-H protons.

The second structure, Ib, is a challenging one to refute. In order to accomplish the formation of this compound, rearrangement of the isocyanide ligand group would have to occur; it is difficult to see how this would occur mechanistically. A second disadvantage for this structure is that the only reasonable canonical structure requires that the complex be highly polar; *i.e.*

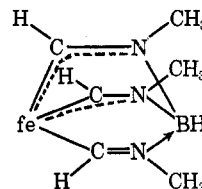


Nevertheless this structure would provide the observed nmr equivalence of CH₃ and CH groups. The third possible structure, Ic, can be thought of as analogous to that of the compound formed on hydrazine reduction of Pt(CNCH₃)₄²⁺.^{26,27} It does require BH addition to the coordinated isocyanide group in the opposite direction and does give a structure less satisfactory on steric grounds.

Interestingly, the reaction which may be the closest precedent to this type of addition reaction was observed by us several years ago. The reaction of C₅H₅M(CO)₃[(C₆H₅)₃P]⁺ and sodium borohydride gave C₅H₅M(CO)₂[(C₆H₅)₃P]CH₃.⁷ The product formation, involving reduction of a carbonyl to a methyl group, probably occurred by BH addition to the C≡O of the coordinated carbonyl. In that work the reaction proceeded further however and no isolable intermediate was identified. This perhaps is a reflection of the higher stability of the boron-nitrogen heterocycles *vs.* the yet unknown analogous boron-oxygen complex.

An analogous reaction, in that it involves BH addition to coordinated isocyanide groups, occurs between C₅H₅-Fe(CNCH₃)₃⁺ and BH₄⁻ giving C₅H₅Fe(CHNCH₃)₃-BH. The yellow covalent product exhibits no terminal ν_{C=N} in the infrared, and in addition the proton nmr spectrum contains three resonances of relative intensities 5:9:3. The single proton not observed in this spectrum is ascribed to a hydrogen remaining bonded to the boron, and as in the earlier examples, the multiplicity and anticipated broadness of this resonance has obscured its presence. There is a ν_{BH} absorption in the infrared spectrum of this compound and the ¹¹B spectrum occurs as a doublet, as expected. Structure Ib seems most appropriate for this complex. The spectroscopic data seem clearly to rule out an alternative structure in which addition to only two isocyanide ligands has occurred, to give a complex

like Ia with isocyanide substituted for terminal carbonyl. The proton nmr spectrum suggests that a delocalized structure would be most appropriate, to explain the singlet CH₃ and CH resonances at τ 6.7 and -2.0. One of several canonical forms is



In the structures proposed for these borohydride addition products, the BH₂ (or BH) groups would not be a part of the partially delocalized ring system of necessity, as the boron atom is four-coordinate and thus coordinately saturated. This fact, in turn, suggested that at least for the monocyclic compounds such as C₅H₅Fe(CO)(CHNCH₃)₂BH₂, abstraction of a hydride ion might be possible giving a ring system fully delocalized over all six atoms. In an attempt at such a reaction, this iron complex and the common hydride abstracting agent (C₆H₅)₃C⁺BF₄⁻ led unexpectedly to C₅H₅Fe(CO)(CHNCH₃)₂BF₂, in which exchange of fluorine for hydrogen in the BH₂ group had been accomplished. The same reaction with C₅H₄-CH₃Mn(NO)(CHNCH₃)₂BH₂ gave the complex C₅H₄-CH₃Mn(NO)(CHNCH₃)₂BF₂. Both iron and manganese complexes had properties substantially similar to their BH₂ analogs, except for those spectroscopic properties associated with BF₂ and BH₂ groups. In both reactions triphenylmethane was an isolated product. This suggests that perhaps the route to these new complexes may in fact be *via* the expected cationic intermediate but that this in turn is a sufficiently strong fluoride acceptor to abstract F⁻ from the counterion BF₄⁻.

A possible alternate route to these compounds, involving exchange of BH₂ by BF₂ (from BF₄⁻), can be discounted since the products are not formed from starting material and NaBF₄ under the same conditions. Indirectly, this hypothesis is also supported by the failure to accomplish this reaction with C₅H₅Fe-(CHNCH₃)₃BH which presumably would not readily lose a hydride ion since the tricyclic geometry of the ligand plus metal would force boron to remain in a trigonal geometry and would prevent any substantial delocalization of electrons to boron.

Acknowledgments.—We are pleased to acknowledge support of this work from the Petroleum Research Fund (as a graduate fellowship to J. P. S.) and from the National Science Foundation (Grants GP-8140 and GP-17207). The departmental mass spectrometer (MS-902) and HA-100 nmr spectrometer used in this work were obtained on recent NSF instrument grants to the department. Professor D. F. Gaines of this department provided the ¹¹B nmr spectra.

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