such reduction wave was observed. There are a number of ways by which $CrNC^{2+}$ could escape polarographic detection, for instance, reoxidation of the reduction product of $CrNC^{2+}$ to $CrCN^{2+}$ could cancel the wave of $CrNC^{2+}$.

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The Synthesis of 1,2-Benzocycloheptatrieneiron Tricarbonyl and Benzotropeniumiron Tricarbonyl Tetrafluoroborate

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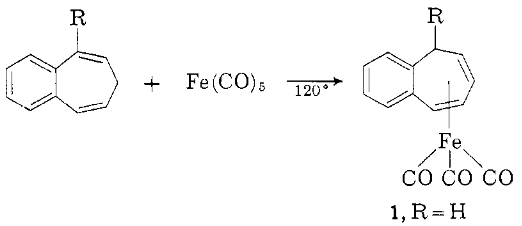
The tendency for iron to form tricarbonyl complexes with conjugated dienes leads to an interesting question as to the products which would arise from the reaction of 3,4-benzocycloheptatriene with iron pentacarbonyl. There are no examples of an iron carbonyl fragment complexed to a benzenoid aromatic system. The nonbenzenoid aromatic hydrocarbon azulene does form a diiron pentacarbonyl derivative.[1] However, crystal structure data indicate that the π electrons of the five- and seven-membered rings of azulenediiron pentacarbonyl are localized within the respective rings.[2] Isomerization of the 3,4-benzocycloheptatriene to the 1,2-benzo isomer in the presence of iron pentacarbonyl would lead to a simple diene which would be expected to form a tricarbonyl complex. This latter path is correct as evidenced by the facile reaction of both 3,4-benzocycloheptatriene and 5-methyl-3,4-benzocycloheptatriene with iron pentacarbonyl at 120° to yield 1,2-benzocycloheptatrieneiron tricarbonyl (1) and 7-methyl-1,2-benzocycloheptatrieneiron tricarbonyl (2), respectively.



1, R = H
2, R = CH_3

The structures can be verified by the nmr spectra of the compounds. The nmr spectrum of 1,2-benzocycloheptatrieneiron tricarbonyl (**1**) is shown in Figure 1. The two-hydrogen multiplet at τ 4.55 is assigned to the 4,5 hydrogens and the two multiplets at τ 6.2 and 6.6 are assigned to the 3 and 6 hydrogens, respectively. The assignments are based on the generally observed chemical shifts of cyclic dieneiron tricarbonyls.[3] The alternate structure of 3,4-benzocycloheptatrieneiron tricarbonyl is excluded by the nmr spectrum since this latter structure should exhibit only two types of vinyl hydrogens. The assigned structure for 7-methyl-1,2-benzocycloheptatrieneiron tricarbonyl is established by the similarity of the nmr spectrum to that of 1,2-benzocycloheptatrieneiron tricarbonyl and the fact that the methyl appears as a doublet (J = 6.7 cps).

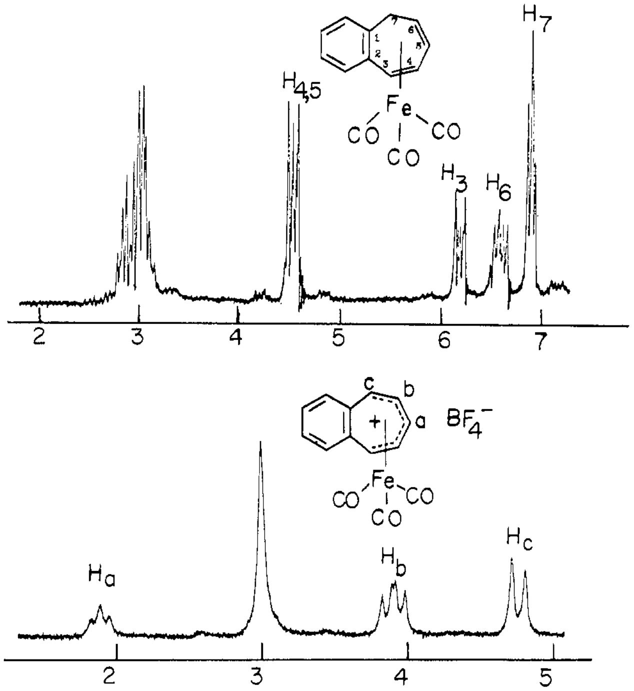


Figure 1.—Nmr spectrum of 1,2-benzocycloheptatrieneiron tricarbonyl.

The fact that cycloheptatrieneiron tricarbonyl will not undergo hydride abstraction when treated with triphenylcarbonium tetrafluoroborate, but reacts by addition instead,[3,4] can be explained by the preference of the iron tricarbonyl group to favor a pentadienium ion ligand which has an empty nonbonding π orbital available for back bonding, rather than a tropenium ion ligand which has only unfilled antibonding π orbitals.[5] However, 1,2-benzocycloheptatrieneiron tricarbonyl (**1**) could undergo hydride abstraction to give a complex more nearly resembling a benzenepentadienium ligand with little interaction between the benzene and pentadienium π systems rather than one electronically resembling a benzotropenium ligand. Treatment of 1,2-benzocycloheptatrieneiron tricarbonyl with tri-

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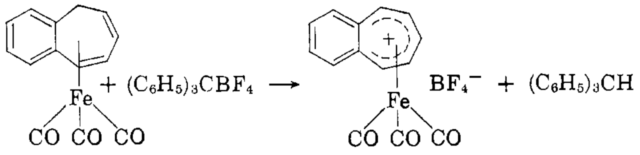
phenylcarbonium tetrafluoroborate leads to a rapid hydride abstraction reaction to give ion **3**. The nmr spectrum of this ion is shown in Figure 1 and deviates markedly from that of the benzotropenium ion.[6] Although it would be anticipated that the chemical shifts would be different for ion **3** and benzotropenium ion, the differences are large and lead to the conclusion that the electron distributions are quite different in the two species.



3

In going from benzocycloheptatriene to benzotropenium ion, the seven-membered-ring hydrogens shift downfield by *ca.* 2.5 ppm, and the benzene hydrogens shift downfield by *ca.* 1.5 ppm.[6] In going from 1,2-benzocycloheptatrieneiron tricarbonyl to ion **3**, the seven-membered-ring hydrogens shift downfield by *ca.* 2 ppm, but the benzene ring hydrogens remain essentially unchanged. These data indicate that the positive charge of ion **3** is localized on the five carbon atoms of the seven-membered ring which are not common to both rings, with little or no leakage of the charge into the benzene ring. Thus the iron atom does cause the ligand ion to appear as an independent benzenepentadienium cation system with a nonbonding empty π orbital available for back-bonding of iron electrons, rather than a benzotropenium ion ligand which would have only antibonding π orbitals available[7] for this purpose.

Finally, the pK_{R^+} of ion **3** (4.27), which is very near the corresponding value for tropeniumiron tricarbonyl ion (4.5) and cycloheptadieniumiron tricarbonyl (4.7),[8] appears to reflect the stability of a typical dieniumiron tricarbonyl cation rather than the difference in pK_{R^+} of tropenium ion (4.7) and benzotropenium ion (1.7).[9]

Experimental Section

The nmr spectra were taken on a Varian HA-100 nmr spectrometer. The ultraviolet spectra were determined on a Cary Model 14 recording spectrophotometer. Infrared spectra were determined on a Perkin-Elmer Model 337 ir spectrometer, and the carbonyl absorptions were determined on a Beckman IR 7 instrument. The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

1,2-Benzocycloheptatrieniron Tricarbonyl.—3,4-Benzocycloheptatriene[10] (1.00 g, 7.05 mmol) and iron pentacarbonyl (3.00 g, 15.31 mmol) were heated to 120° for 72 hr under an inert atmosphere. After cooling the mixture, 30 ml of hexane was added and the solution was filtered. The resulting yellow solution was concentrated to a yellow oil by the means of a rotary evaporator. The oil was molecular distilled at room temperature to remove any unreacted starting material. The residue was then sublimed at 100° (0.025 mm) to give yellow crystals of 1,2-benzocycloheptatrieneiron tricarbonyl (1.322 g, 66% yield based on olefin); mp 82.0–82.5°. *Anal.* Calcd for $C_{14}H_{10}FeO_3$: C, 59.19; H, 3.55. Found: C, 59.17; H, 3.59. The infrared spectrum of the complex shows carbonyl bands at 2055, 1988, and 1974 cm^{-1} (CCl_4 solution). Other bands in the spectrum occur at 3035 (w), 2960 (s), 2915 (m), 1501 (s), 1468 (s), 1450 (m), 1250 (m), 1183 (w), 1162 (m), 1150 (sh), 1098 (m), 1031 (m), 988 (w), 932 (m), 882 (m), 728 (m), 696 (s), 617 (s), and 562 (m) cm^{-1}. The ultraviolet spectrum of $C_{11}H_{10}Fe(CO)_3$ shows maxima at 228 mμ (ϵ 33,500) and a shoulder at 283 mμ (ϵ 13,000). The nmr spectrum of the complex in carbon tetrachloride and acetonitrile (50:50) mixture shows resonances at τ 3.00 (benzene ring, multiplet), 4.63 ($H_{4,5}$ septet), 6.36 (H_3, pentet), 6.58 (H_6, multiplet), and 6.90 (H_7, triplet) with respect to TMS. Relative intensities were 4:2:1:1:2, respectively.

1,2-Benzocycloheptatriene[10] (0.50 g, 3.52 mmol) and iron pentacarbonyl (1.50 g, 7.66 mmol) were heated to 120° for 36 hr under a nitrogen atmosphere. After cooling the mixture, 40 ml of hexane was added and then filtered. The resulting solution was evaporated, leaving a yellow residue. The residue was dissolved in 5 ml of hexane and allowed to crystallize. The solution was filtered and the yellow precipitate was collected (0.782 g, 78% yield); mp 82.0–82.5°. A mixture melting point with 1,2-benzocycloheptatrieneiron tricarbonyl was 82.0–82.5°. The nmr, infrared, and ultraviolet spectra were the same; therefore the complex was assumed to be 1,2-benzocycloheptatrieneiron tricarbonyl.

Benzotropyliumiron Tricarbonyl Tetrafluoroborate.—1,2-Benzocycloheptatrieneiron tricarbonyl (1.00 g, 3.52 mmol) dissolved in 10 ml of methylene chloride was added to a solution of triphenylmethyl tetrafluoroborate (1.25 g, 3.79 mmol) in 10 ml of methylene chloride. The product precipitated immediately and the reaction was assumed to be complete after 30 min. The precipitate was filtered and washed with a few milliliters of methylene chloride. The yellow needles of benzotropyliumiron tricarbonyl tetrafluoroborate (1.20 g, 92.2% yield) were recrystallized from acetonitrile. The compound did not exhibit a melting point, but only darkened above 230°. *Anal.* Calcd for $C_{14}H_9FeO_3BF_4$: C, 45.46; H, 2.45. Found: C, 45.19; H, 2.53. The infrared spectrum of the salt in KBr shows carbonyl bands at 2139 and 2082 cm^{-1}. Other bands in the spectrum (cm^{-1}) occur at 2975 (m), 2945 (s), 1635 (m), 1600 (sh), 1500 (sh), 1480 (m), 1440 (sh), 1410 (m), 1380 (sh), 1290 (sh), 1272 (m), 1171 (m), 1160 (sh), 1060 (b), 990 (m), 903 (m), 867 (m), 766 (s), 638 (m), 598 (s), 583 (s), and 557 (s). The ultraviolet spectrum shows maxima at 232 mμ (ϵ 22,300), 282 mμ (ϵ 16,500), and 330 mμ (ϵ 6850). The nmr spectrum of the salt in trifluoroacetic acid shows resonance at τ 1.80 (H_1, triplet, 6.5-cycle separation), 3.06 (benzene ring singlet), 3.85 ($H_{2,7}$, double doublets), and 4.75 ($H_{3,6}$, doublet, 9-cycle separation) with respect to TMS. Relative intensities were 1:4:2:2, respectively. The following coupling constants were found: $J_{12} = 6.5$ cps, $J_{17} = 6.5$ cps, $J_{23} = 9$ cps, and $J_{67} = 9$ cps.

1-Methyl-2,3-benzocycloheptatrieneiron Tricarbonyl.—3-Methyl-3,4-benzocycloheptatriene[11] (1.00 g, 6.41 mmol) and iron pentacarbonyl (3.00 g, 15.31 mmol) were heated to 120° for 72 hr under an inert atmosphere. After cooling the mixture, 30 ml of hexane was added and the solution was filtered. The resulting yellow solution was evaporated on a rotary evaporator to give yellow oily crystals. The yellow crystals were dissolved in a minimum amount of hexane and allowed to crystallize at 0°. The product was purified by sublimation to yield yellow crystals of 1-methyl-2,3-benzocycloheptatrieneiron tricarbonyl (1.824 g, 95.0% yield); mp 89.0–90.0°. *Anal.* Calcd for $C_{15}H_{12}FeO_3$: C, 60.43; H, 4.05. Found: C, 60.23; H, 3.96. The infrared spectrum of the complex shows carbonyl bands at 2049, 1980, and 1972 cm^{-1} (CCl_4 solution). Other bands in the spectrum occur at 3070 (w), 3020 (m), 2950 (s), 2910 (m), 2850 (m), 1495

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(s), 1465 (s), 1450 (m), 1248 (m), 1185 (w), 1160 (m), 1148 (sh), 1100 (m), 1031 (m), 984 (m), 930 (m), 885 (m), 730 (m), 695 (s), 617 (s), and (m) 560 cm^{-1}. The ultraviolet spectrum of the complex in hexane shows a maximum at 230 mμ (ε 33,000) and a shoulder at 285 mμ (ε 12,500). The nmr spectrum of the complex in carbon tetrachloride, acetonitrile, and tetramethylsilane (60:35:5) mixture shows resonances at τ 3.00 (benzene ring, multiplet), 4.58 ($H_{4,5}$, pentet), 6.32 (H_3, pentet), 6.73 (H_6, septet), about 6.9 (H_7, multiplet), and 8.77 (CH_3, doublet) with respect to TMS. Relative intensities were 4:2:1:1:1:3.

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Transition Metal Carbonyl Complexes of the Constrained Phosphite Esters: 4-Methyl-, 4-Ethyl-, and 4-Propyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

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The mono- and disubstituted complexes of various metal carbonyls with $P(OCH_2)_3CR$, where R = CH_3 and C_2H_5, have been previously reported,[2,3] and the formation of *cis*-$Mo(CO)_3(P(OCH_2)_3CCH_3)_3$ has been observed in kinetic studies.[4] The strong π-bonding ability of the ligands[2] leads one to predict that trisubstituted complexes of the type $M(CO)_3L_3$, where M = Cr, Mo, or W and L = phosphite esters, should be readily obtainable.

The proton nmr spectra of the disubstituted compounds of the methyl and ethyl bicyclic phosphites display interesting features of phosphorus spin-spin coupling.[2,3] Previous reports in the literature[5,6] suggest that in disubstituted compounds such coupling is observed only when the phosphorus ligands are in the *trans* position. If such is the case, one would expect to observe proton absorptions having similar shapes for compounds of the types *cis*-$M(CO)_4L_2$ and *cis*-$M(CO)_3L_3$. The effect of the length of the alkyl chain on the coordination properties of ligands of the type $P(OCH_2)_3CR$ may be evaluated by comparing the properties of the compounds reported previously where R = CH_3 and C_2H_5 with those described herein where R = C_3H_7. The solubility in organic solvents of the complexes containing $P(OCH_2)_3CR$ ligands is enhanced by the larger C_3H_7 group, making their characterization in solution easier.

Experimental Section

The infrared spectra were obtained in chloroform solutions and recorded on a Perkin-Elmer Model 21 double-beam spectrometer using sodium chloride optics. The proton nmr spectra were recorded for approximately 15% chloroform solutions on a Varian Associates Model A-60 spectrometer using tetramethylsilane as an internal standard. Carbon and hydrogen compositions were ascertained by combustion. Yields were calculated on the basis of the limiting reagent.

Iron pentacarbonyl was purchased from Antara Chemical Co., chromium hexacarbonyl was purchased from Pressure Chemical Co., and molybdenum and tungsten hexacarbonyls were gifts from Climax Molybdenum Co. The bicyclic phosphite ligands,[7,8] $C_7H_8Cr(CO)_3$[9] and $C_7H_8Mo(CO)_3$,[10] were prepared by methods described elsewhere.

A slightly greater mole ratio of ligand to metal carbonyl or $C_7H_8M(CO)_3$ than theoretically necessary to yield the di- and trisubstituted products was used while a slightly smaller ratio was used for the monosubstituted complexes. The trisubstituted chromium and molybdenum complexes were prepared from the appropriate cycloheptatriene compound. The solvent used in the preparation of all trisubstituted complexes of chromium, molybdenum, and tungsten was methylcyclohexane, diethyl ether, and toluene, respectively. Dioxane was used for $Fe(CO)_3L_2$, $W(CO)_4L_2$, and $W(CO)_5L$ while the remaining complexes were prepared with *n*-octane.

Two general methods were used in the preparation of the complexes listed in Table I. In method A, a mixture of metal carbonyl or cycloheptatriene metal carbonyl and ligand in approximately 30 ml of solvent was refluxed under a helium flush with magnetic stirring for the indicated time. Compounds were isolated by suction filtration and were washed on the filter with *n*-pentane, hexane, or anhydrous diethyl ether. In some cases, it was necessary to reduce the volume of the mixtures by vacuum evaporation in order to obtain a filterable product. After purification was effected according to the method listed in Table I, all compounds were dried under vacuum.

In method B, a mixture of metal carbonyl, ligand, and 50 ml of solvents was placed in a quartz flask. Irradiation with ultraviolet light (200-W Hanovia Model 654A-10) was carried out for the time indicated under a flush of helium with magnetic stirring. The mixtures were filtered by suction to remove solid decomposition products and then treated in the same manner given in method A. In the preparation of some compounds, mixtures of carbonyl complexes of varying degrees of substitution were obtained. By employing chromatography and/or fractional crystallization, it was possible to obtain pure compounds. As a result, both isomers of two complexes could be prepared using a single set of reaction conditions.

Preparative method A was employed for all of the reactions except for the tungsten complexes and the disubstituted iron complex for which method B was used. Analytical data for the compounds are presented in Table I.

Decomposition of the solid mono- and disubstituted complexes is observed after several days to weeks upon standing in air while solutions are usually stable for several hours or more. The colorless trisubstituted complexes appear to be less stable than the disubstituted complexes.

Results and Discussion

The infrared spectra (Table II) confirm the expectation that compounds of the type $M(CO)_3L_3$ can be prepared. The number of observed bands in the CO stretching region, two of medium intensity, support the postulate that these compounds are the *cis* isomers.

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