Volume 14
Number 2
February 1975

Inorganic Chemistry

Contribution from the Department of Chemistry,
Florida State University, Tallahassee, Florida 32306

Metal Carbonyl–Trifluorophosphine Systems. XIIA. Methylbutadienetricarbonyliron(0) Systems—Preparation and Vibrational Analysis

MARIANNA ANDERSON BUSCH and RONALD J. CLARK*

Received May 10, 1974 AIC40298G

Methyl-substituted butadienetricarbonyliron(0) complexes have been prepared by photochemical reaction of the diene with $Fe(CO)_5$ or by thermal reaction with $Fe_2(CO)_9$. Careful examination of the infrared spectra of these complexes shows that the carbonyl stretching force constants of $C_4H_6Fe(CO)_3$, calculated from an energy-factored force field, are altered in an additive way depending upon the number of methyl groups and their position of substitution into the butadiene. The K_1 vibrational force constants for the unique, apical carbonyls show good correlation with the HMO ψ_2 and ψ_3 diene orbitals. The K_2 force constants for the basal carbonyls correlate with the absolute number of methyl groups on the butadiene ligand. Phosphorus trifluoride substitution can be effected photochemically in these complexes. The individual (diene)$Fe(PF_3)_x(CO)_{3-x}$ species are isolated by glpc and readily characterized. The infrared spectra of the phosphine complexes show no evidence for more than one of the possible isomers in the square-based pyramidal structure. The PF_3 group appears to prefer the apical position.

Introduction

The similarity between the properties of metal carbonyls and their phosphorus trifluoride analogs has been demonstrated for a large number of cases.[1] This similarity is so great that in many complexes PF_3 and CO can undergo nearly random exchange. Thus, sequential replacement of CO by PF_3 in a metal carbonyl $M(CO)_n$ generally yields all possible compositions of the type $M(PF_3)_x(CO)_{n-x}$. If more than one isomer can result from each degree of PF_3 substitution, all possible isomers are often observed as well.

Previous investigations of trifluorophosphine substitution into butadiene-[2] and 1,3-cyclohexadieneiron tricarbonyl,[3] $C_4H_6Fe(CO)_3$ and $C_6H_8Fe(CO)_3$, have revealed some significant differences between the CO and PF_3 ligands. If the two groups are quite similar as ligands, isomer populations should be determined by an essentially statistical distribution of the ligands over all types of coordination sites. However, it was found that the PF_3 groups prefer the apical over the basal position in the square-based pyramidal structure.[4] In the butadiene system, only the isomers based on this preference are observed.[2] Site preference in the cyclohexadiene system is less pronounced, but PF_3 substitution is still far from random.[3]

The investigation of a series of other dieneiron carbonyl–trifluorophosphine systems was undertaken in order to help clarify the factors determining site preference in these complexes. The presence of a methyl group is not expected to alter the electron distribution within the diene very drastically, and the resulting dieneiron complexes are likely to have structures analogous to the previously examined butadiene and cyclohexadiene complexes. Since a large number of methyl-substituted butadienes are available, it will also be possible to examine the effect of different dienes on the carbonyl force constants.

Experimental Section

The dieneiron tricarbonyls were prepared by two methods.

Method I. A 1–5 ml amount of the appropriate diene, about 5 ml of $Fe(CO)_5$ (Alfa Inorganics), and around 10 ml of hexane were mixed in a 500-ml cylindrical flask equipped with a vacuum stopcock. Air was removed by vacuum pumping at low temperatures, and the flask was irradiated at 0° by an AH-6 1000-W General Electric uv lamp. The flask, indented at one end so as to fit around the lamp, was rotated during irradiation, exposing the reaction mixture as a thin film. After several hours, the solvent, excess diene, and unreacted $Fe(CO)_5$ were removed by vacuum distillation at −30°, and the product was further purified by glpc.

Method II. A 5–10-ml amount of the appropriate diene and an excess of $Fe_2(CO)_9$[5] were mixed in 100 ml of anhydrous ether in a 250-ml round-bottomed flask fitted with an ice-water-cooled condenser. The reactants were heated at 40–45° under dry nitrogen gas for about 1.5 hr, or until the $Fe_2(CO)_9$ had disappeared to give a dark brown solution. Excess solvent was removed by vacuum distillation at −30°, and the product was further purified by glpc.

Phosphorus trifluoride was obtained from Ozark-Mahoning. It was further purified by passing it slowly through a 36-in. water tower packed with glass beads, followed by distillation from a −126° methylcyclohexane slush bath to remove traces of water.

The PF_3 compounds were prepared by irradiating 0.5–1 ml of the appropriate dieneiron tricarbonyl in 5–10 ml of hexane at 0° in a 500-ml cylindrical flask containing PF_3 at a pressure of about 600 Torr. The progress of the reaction as a function of reaction time was followed by periodically removing samples through a septum and examining the infrared spectrum of the solution in the carbonyl region. The rate of PF_3 substitution could be considerably increased by rotating the flask and exposing the liquid phase as a thin film. Irradiation times of 2–6 hr were usually sufficient to yield (diene)$Fe(PF_3)_x(CO)_{3-x}$ mixtures in which appreciable amounts of the $x = 1$, 2, and 3 species were present. The bulk of the solvent was then removed by vacuum distillation at −30°, and the products were isolated by glpc.

A Varian-Aerograph A-700 Autoprep chromatograph was used to isolate the complexes. Copper columns, 0.25 in. in diameter, were packed with 15% Dow Corning DC-702 silicone oil on Chromasorb FB. Column lengths varied from 0.5 to 5 m, and column temperatures ranged from 60 to 118° depending on the system. No attempt was made to obtain more pure material than that required for physical measurements.

(1,3-Butadiene)$Fe(PF_3)_x(CO)_{3-x}$. 1,3-Butadieneiron tricarbonyl was obtained from Alfa Inorganics. It was shown by glpc to be sufficiently pure for use without further purification. The $x = 1$, 2, and 3 species were isolated at 80° on a 4-m column as before.[2]

(2,3-Dimethyl-1,3-butadiene)Fe(PF$_3$)$_x$(CO)$_{3-x}$. For $x = 0$, irradiation of 2,3-dimethylbutadiene (Aldrich) with Fe(CO)$_5$ for 6 hr according to method I was followed by isolation of the complex on a 4-m column at 112°. The monophosphine was isolated at 85° on a 1-m column, and the di- and triphosphines were isolated at 95° on a 5-m column.

(Isoprene)Fe(PF$_3$)$_x$(CO)$_{3-x}$. For $x = 0$, irradiation of isoprene (Aldrich) with Fe(CO)$_5$ for 2–4 hr according to method I was followed by isolation of the complex on a 2-m column at 90°. The monophosphine was isolated at 90° on a 2-m column, and the di- and triphosphines were separated at 90° on a 5-m column.

(*trans,trans*-2,4-Hexadiene)Fe(PF$_3$)$_x$(CO)$_{3-x}$. For $x = 0$, irradiation of *trans,trans*-2,4-hexadiene (Aldrich) with Fe(CO)$_5$ for 1 hr according to method I was followed by isolation of the complex on a 2-m column at 90°. The mono- and diphosphines were isolated at 82° on a 2-m column. For irradiation times of up to 6 hr the triphosphine was formed in only very small amounts (detected as small impurity peaks in the mass spectrum of the diphosphine). It was not isolated or studied.

(*trans*-1,3-Pentadiene)Fe(PF$_3$)$_x$(CO)$_{3-x}$. *trans*-1,3-Pentadieneiron tricarbonyl (obtained from Alfa Inorganics) was shown by glpc to be sufficiently pure for use without further purification. The phosphine species were isolated on 2- and 5-m columns at 89°.

(*cis*-1,3-Pentadiene)Fe(PF$_3$)$_x$(CO)$_{3-x}$. Treatment of commercial 1,3-pentadiene (Aldrich mixture of isomers) with maleic anhydride according to the method of Frank, Emmick, and Johnson[6] produced a fraction shown by glpc to be free of the trans isomer. This fraction was irradiated for 0.5–1 hr with Fe(CO)$_5$ according to method I or refluxed with Fe$_2$(CO)$_9$ according to method II. Both procedures produced a mixture of products composed of about 95% *cis*-1,3-pentadieneiron tricarbonyl and about 5% of a complex with a glpc retention time and infrared and proton nmr spectra identical with those of *trans*-1,3-pentadieneiron tricarbonyl purchased from Alfa Inorganics. The cis and trans complexes were isolated from one another by glpc at 87° on a 2-m column.

For $x = 1$, 2, and 3, the *cis*-1,3-pentadieneiron tricarbonyl and PF$_3$ were irradiated for 0.5–6 hr. As shown by infrared and glpc, both the (*trans*- and *cis*-1,3-pentadiene)Fe(PF$_3$)$_x$(CO)$_{3-x}$ systems were produced, perhaps a result of isomerization of the cis species to the trans isomers.[7] The monophosphines of both isomers were separated as a single group from all other species by glpc on a 2-m column at 90°. The cis monophosphine was then isolated from the trans at 93° on a 4-m column. The cis diphosphine was isolated at 93° on a 5-m column. It was not possible to isolate the cis triphosphine from a mixture of the di- and triphosphines of the trans complex. This mixture was satisfactory for fluorine nmr studies as the resonances do not overlap.

(2,4-Dimethyl-1,3-pentadiene)Fe(PF$_3$)$_x$(CO)$_{3-x}$. For $x = 0$, irradiation of tetramethylallene (Aldrich) with Fe(CO)$_5$ for 0.5 hr according to method I produced a mixture composed of tetramethylalleneiron tetracarbonyl[8] and 2,4-dimethyl-1,3-pentadieneiron tricarbonyl in a 2:1 ratio. Longer irradiation times increased the percentage of tricarbonyl. Refluxing tetramethylallene with Fe$_2$(CO)$_9$ according to method II produced mainly tricarbonyl. Isolation of the tricarbonyl was accomplished by glpc at 100° on a 0.5-m column. The monophosphine was isolated by glpc at 118° on a 4-m column. The di- and triphosphines could not be separated from each other and were studied as mixtures.

Other Tricarbonyls. Irradiation of 4-methyl-1,3-pentadiene (Aldrich) and Fe(CO)$_5$ for 0.5–1 hr according to method I yielded three isomeric tricarbonyls which, in order of increasing glpc retention time, were identified as 2-methyl-*trans*-1,3-pentadieneiron tricarbonyl, 2-methyl-*cis*-1,3-pentadieneiron tricarbonyl, and 4-methyl-1,3-pentadieneiron tricarbonyl. These complexes were isolated at 92° on a 2-m column.

Some isomerization of the 4-methyl-1,3-pentadiene complex to the two other isomers appeared to take place at 92°. Rechromatographing the complex at 60° on a 0.5-m column yielded this tricarbonyl free of the other isomers.

Irradiation of *cis,trans*-2,4-hexadiene (Aldrich) and Fe(CO)$_5$ for 0.5–1 hr according to method I yielded *cis,trans*-2,4-hexadieneiron tricarbonyl. Purification was accomplished by glpc at 90° on a 2-m column.

The *cis*-1,3-pentadienediphosphine and all isolable triphosphine complexes are yellow solids at room temperature. The other complexes are yellow liquids.

With the exception of 4-methyl-1,3-pentadieneiron tricarbonyl, all carbonyl and trifluorophosphine complexes are relatively air stable and can be stored in sealed tubes at −17° in the absence of air and light for periods of several months to 1 year without decomposition or disproportionation. Solutions for nmr study, sealed in the absence of air, showed a similar stability. Pure 4-methyl-1,3-pentadieneiron tricarbonyl and solutions of this complex showed noticeable deterioration after storage periods of several weeks.

Infrared spectra of the complexes in hexane solution were recorded on a P-E 521 spectrometer, calibrated once each day in the carbonyl region with gaseous DCl[9] on an expanded wave number scale. Multiple determinations suggest that the error in the values of the carbonyl bands is about ±0.3 cm^{-1}. The variation in the force constants calculated from these bands is about ±0.01 mdyn/Å.

Proton and fluorine nmr spectra were recorded on a Bruker HFX-90 spectrometer equipped with a variable-temperature unit and operating at 90 and 84.66 MHz, respectively. The temperature controller was calibrated by a thermocouple in a separate nmr tube. The temperature readings are believed accurate to at least ±3°. Near room temperature the accuracy is probably ±2° or better.

Chemical shifts were measured relative to lock signals. Solvent and reference systems included the following: (1) for low-temperature proton studies, CS$_2$ as solvent with CHCl$_3$ as internal reference and lock; (2) for low-temperature fluorine studies, isopentane as solvent with the high-field peak of the CHFCl$_2$ fluorine doublet as primary internal reference and lock and CFCl$_3$ as secondary internal reference; (3) for high-temperature fluorine studies, toluene as solvent with α-trifluorotoluene as internal reference and lock. The value of J_{HF} in CHFCl$_2$ is constant to within ±0.5 Hz over the temperature ranges studied. Data taken in other solution systems did not differ significantly from data taken in the solutions listed above.

Mass spectra were determined at 70 eV on a Nuclide 120 90-G 1.5 instrument. For 4-methyl-1,3-pentadieneiron tricarbonyl, the inlet port temperature was kept at or below 60°.

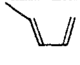
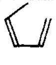
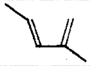
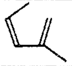
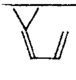
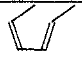
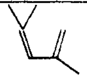
Results

A series of dieneiron tricarbonyls is readily prepared by a photochemical reaction of dienes with Fe(CO)$_5$ or by a thermal reaction of dienes with Fe$_2$(CO)$_9$. Isomerization of the diene upon complexation sometimes occurs, usually involving a cis methyl group on the terminal diene carbon changing to a trans position. This phenomenon has been previously reported.[7] Phosphorus trifluoride substitutes photochemically at 0° into the tricarbonyl for every case attempted, yielding all possible compositions of the type (diene)Fe(PF$_3$)$_x$(CO)$_{3-x}$. The compounds of the composition $x = 0$–3 can be identified by several techniques.

(1) Mass Spectroscopy. After isolation, the tricarbonyls and the components of the PF$_3$ reactions were examined by mass spectroscopy. The parent ion molecular weight for each of the species agrees with that expected. In general, metal–carbonyl and metal–trifluorophosphine mass spectra are characterized by a successive loss of CO[10,11] and PF$_3$[2,3,12] from the molecular ion. These peaks are the main features of the spectra of these complexes in the high mass region. The most intense peaks in the spectrum of the parent complex as well as in the PF$_3$-substituted species correspond to the ions [(diene)Fe]$^+$ and [Fe]$^+$.

(2) Proton Nmr. The proton peak positions for many of these tricarbonyls have been reported elsewhere[7,11] and agree with spectra observed in this study. For complexes not previously reported, proton nmr is extremely valuable for determining the structure of the diene. There are three types of protons: those on the central carbons 2 and 3, those on the terminal carbons 1 and 4 in an outer or trans configuration, and those on the terminal carbons in an inner or cis configuration. Each of these types of protons has a very characteristic chemical shift and shows consistent variations as methyl groups are introduced.[7] In addition, the methyl resonances were also

Table I. Observed Infrared Spectra of the Diene–Fe(CO)$_3$ Species in the Carbonyl Region (cm^{-1})

				
A′(1)	2055.9 s	2049.7 s	2052.8 s	2043.9 s
A′(2)	1990.0 s	1984.4 s	1986.5 s	1977.4 s
A″	1980.1 s	1972.0 s	1975.3 s	1969.0 s
A′*(1)	2044.1 sh^a	2036.8 sh^a	2039.9 sh^a	2034.2 sh^{a,d}
A′*(2)	1957.0 w^a	1952.0 w^a	1954.1 w^a	1942.8 w^a
A*	2047.1 sh^a	2041.5 sh^a	2043.9 sh^a	2034.2 sh^{a,d}
A*	1946.0 w^{a,b}	1938.5 w^{a,b}	1941.7 w^{a,b}	1935.2 w^{a,b}
				
A′(1)	2049.6 s	2050.6 s	2047.0 s	2047.8 s
A′(2)	1983.8 s	1984.7 s	1981.0 s	1982.0 s
A″	1974.2 s	1976.7 s	1970.5 s	1973.0 s
A′*(1)	2039.0 sh^a	2041.3 sh^{a,d}	2035.1 sh^a	2036.1 sh^a
A′*(2)	1949.7 w^a	1950.4 w^a	1947.5 w^a	1948.1 w^a
A*	2040.9 sh^a	2041.3 sh^{a,d}	2038.1 sh^a	2039.1 sh^a
A*	1941.0 w^{a,c}	1942.7 w^{a,b}	1936.7 w^{a,c}	1938.5 w^{a,b}
				
A′(1)	2044.8 s	2044.6 s	2042.2 s	
A′(2)	1979.6 s	1978.0 s	1977.0 s	
A″	1970.1 s	1970.9 s	1967.2 s	
A′*(1)	2035.3 sh^{a,d}	2035.3 sh^{a,d}	2032.8 sh^{a,d}	
A′*(2)	1943.5 w^{a,c}	1942.3 w^a	1942.3 w^a	
A*	2035.3 sh^{a,d}	2035.3 sh^{a,d}	2032.8 sh^{a,d}	
A*	1937.4 w^{a,c}	1936.6 w^{a,c}	1933.6 w^{a,c}	

[a] ^{13}CO vibration. [b] Twice as intense as the next highest ^{13}CO peak. [c] Broadened or slightly split. [d] A′*(1) and A* vibration observed as single, degenerate peak.

observed to have shifts characteristic of their position on the diene with δ 2.03–2.19 ppm for groups on carbons 2 and 3, δ 1.37–1.55 ppm for groups on carbons 1 and 4 in a trans configuration, and δ 1.10–1.15 ppm for groups on carbons 1 and 4 in a cis configuration. The chemical shifts based on the $CHCl_3$ lock have been converted to a TMS scale using the equation δ(TMS) = 7.23 − δ($CHCl_3$). Coupling constants are similar to those determined for butadieneiron tricarbonyl.[13] Trifluorophosphine substitution does not affect the shifts very significantly, although the splitting patterns are more complex due to additional coupling between the phosphorus atoms and some of the protons.

(3) Infrared Spectra. The infrared spectra of the tricarbonyl and the mono-, di-, and triphosphines for each of the (methylbutadiene)Fe$(PF_3)_x(CO)_{3-x}$ systems show three, two, one, and zero ^{12}CO bands, respectively, in the carbonyl region. The peak positions and relative intensities of these bands are very similar to those observed for the corresponding butadiene complexes.[2]

(4) Order of Formation. The PF_3-substituted complexes are expected to form sequentially as a function of reaction time. Thus the monophosphine should be the first new compound produced, followed by the di- and finally the triphosphine.

(5) Fluorine Nmr. The high-temperature fluorine nmr spectra of the species identified as the mono-, di-, and triphosphines by the above techniques are characteristic of compounds containing one, two, or three PF_3 groups, respectively. These spectra, as well as their temperature dependence, will be discussed in part B of this study (following paper).

Vibrational Analysis and Force Constant Calculations. The infrared spectra in the carbonyl region for the tricarbonyl species are shown in Table I. The presence of three strong ^{12}CO bands suggests that the carbonyls are distorted from C_{3v} symmetry. In addition, the general appearance of the spectra is so similar to that of butadieneiron tricarbonyl[2] that it seems very probable that the complexes have analogous solution structures. Warren and Clark[2] have shown that the best description of this structure is a square-based pyramidal arrangement of the diene and carbonyl groups around the iron such that two carbonyls and the two terminal carbons of the diene form the base and the third carbonyl is at the apex.[4] This gives the Fe(CO)$_3$ groups a local symmetry of C_s with two carbonyls equivalent and one unique.

Based on the arguments used with butadieneiron tricarbonyl[2] and assuming C_s symmetry, there are two stretching force constants and two interaction constants to be calculated.[14] It is not necessary to make any assumptions as to the relative values of these constants as there are sufficient data for this calculation provided the proper assignments can be made. Three ^{12}CO vibrations and one ^{13}CO vibration are required. The validity of each of the possible assignments can be checked by predicting the remaining four ^{13}CO bands, two and sometimes three of which are clearly observable.

Band assignments and calculation of the force constants are relatively straightforward, except for some broadening observed in the lowest frequency ^{13}CO band in the spectra of the complexes of such asymmetric dienes as 2-methyl-*trans*-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, *cis,trans*-2,4-hexadiene, *trans*-1,3-pentadiene, and 4-methyl-1,3-pentadiene. For the last two complexes this broadening is just sufficient for two separate ^{13}CO bands to be resolved. Since none of the band assignments for C_s symmetry predicts two ^{13}CO peaks in this region, the splitting may be caused by a reduction of the local symmetry of the Fe(CO)$_3$ groups from C_s to C_1 due to the influence of the asymmetric diene. If the symmetry of the Fe(CO)$_3$ group is truely C_1, nine weak ^{13}CO bands are expected.[14] However, most of these bands appear to be degenerate, and even the lowest frequency ^{13}CO peak is not split excessively. Therefore, for calculation of the force constants, C_s symmetry for the Fe(CO)$_3$ group in these asymmetric diene complexes would still seem to be a reasonable approximation. Since a comparison of observed ^{13}CO frequencies with those predicted assuming C_s symmetry was just as good as the comparison for those complexes in which strict C_s symmetry is preserved, the approximation appears to be valid. This is

Table II. C–O Stretch–Stretch and Interaction Force Constants for Butadiene- and Several Methylbutadieneiron Tricarbonyls (mdyn/Å)

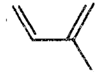
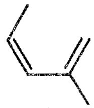
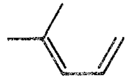
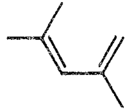
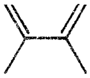
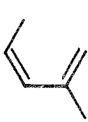
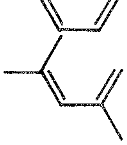
Diene	K_1	K_2	$K_{1,2}$	$K_{2,2'}$
	16.41	16.24	0.37	0.41
	16.27	16.16	0.36	0.42
	16.28	16.19	0.36	0.41
	16.37	16.16	0.38	0.41
	16.33	16.11	0.37	0.41
	16.24	16.10	0.37	0.42
	16.24	16.13	0.36	0.42
	16.13	16.12	0.34	0.45
	16.15	16.08	0.36	0.43
	16.12	16.12	0.35	0.44
	16.13	16.06	0.35	0.43

Table III. Observed and Predicted CO Stretching Force Constants for Several Methylbutadieneiron Tricarbonyls

Values Used in Calculation, mdyn/Å

K	Base value	C_1,C_4 trans substitution	C_1,C_4 cis substitution	C_2,C_3 substitution
K_1	16.41	−0.14	−0.13	−0.04
K_2	16.24	−0.08	−0.05	−0.08

Values Observed and Predicted, mdyn/Å

Diene	K_1		K_2	
	Obsd	Pred	Obsd	Pred
	16.33	16.33	16.11	16.08
	16.14	16.13	16.08	16.08
	16.12	16.14	16.12	16.11
	16.24	16.23	16.10	16.08
	16.24	16.24	16.13	16.11
	16.13	16.14	16.12	16.11
	16.13	16.10	16.06	16.03

particularly true since an unsplit ^{13}CO band can be chosen as the value required in the force constant calculation.

Using the same arguments discussed for the butadiene complex,[2] there are four possible assignments for the frequencies of these complexes. As might be expected from the similarity of their spectra, the best assignment for each of the methylbutadieneiron tricarbonyls is analogous to that of butadieneiron tricarbonyl. This assignment is also the only one which gives $K_1 > K_2$ and $K_{2,2'} > K_{1,2}$, predicted from bonding arguments.[2,15] The force constants for all tricarbonyls are shown in Table II.

The interaction force constants $K_{1,2}$ and $K_{2,2'}$ for the methylbutadiene complexes are all quite similar to those for butadieneiron tricarbonyl and do not vary much with the number or position of the methyl groups. However, an interesting relationship among the stretching force constants K_1 and K_2 is observed. In every case, the presence of a methyl group causes a decrease in both of these constants relative to the values for butadieneiron tricarbonyl. When substitution occurs in two or more positions, the force constants are further decreased, and by a predictable amount. For example, the presence of one methyl on carbon 2 or 3 (isopreneiron tricarbonyl) causes K_1 to decrease 0.04 mdyn/Å relative to the base value of 16.41 determined for butadieneiron tricarbonyl. The presence of one methyl on carbon 1 or 4 in the cis configuration (*cis*-1,3-pentadieneiron tricarbonyl) decreases K_1 by 0.13 mdyn/Å relative to the base value. The additive effect of both methyls should result in a new value of K_1 equal to $16.41 - 0.04 - 0.13 = 16.24$ mdyn/Å. This is precisely the value of K_1 observed for 2-methyl-*cis*-1,3-pentadieneiron tricarbonyl.

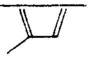
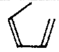
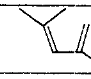
Of the 11 tricarbonyls in Table II, the force constants of the butadiene complex itself and the three monomethylbutadiene complexes are required as base values to determine the effect of a single methyl group in each of the three possible substitution sites. The observed and predicted values of K_1 and K_2 for the seven remaining complexes are shown in Table III.

The standard deviation *s* of a single, observed force constant was estimated to be about ±0.01 mdyn/Å. Three or more observed values are used in each force constant prediction. An estimation of the error *s* for each predicted value, obtained by summing the variances s^2 of each of the observed values used in the calculation,[16] suggests an uncertainty of about ±0.02 mdyn/Å for the predicted force constants. A comparison of the observed and predicted values in Table III shows that, within experimental error, the stretching force constants for all seven tricarbonyls are correctly predicted by assuming an additive effect for the methyl groups.

Infrared spectral data in the carbonyl region for the monophosphine complexes are shown in Table IV. For equivalent carbonyls (C_s symmetry), two ^{13}CO peaks are expected. For nonequivalent carbonyls (C_1 symmetry) a total of four ^{13}CO peaks are expected. Only two ^{13}CO bands are observed in the spectra of all these monophosphines. Two pair of accidently degenerate frequencies are very unlikely. The only other way to produce such a degeneracy would be for the two stretching force constants K_1 and K_2 to be equal. Since they are far from equal in the tricarbonyls, it seems unlikely that they would be equal in the dicarbonyls. On this basis it appears that only the isomer with PF_3 in the apical position exists in sufficient quantities at room temperature to be observed by infrared spectroscopy. This is the same isomer preferred in the butadiene monophosphine.[2] Additional evidence supporting this assignment is provided by fluorine nmr and will be discussed in part B of this study.

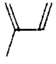
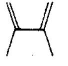
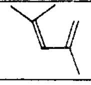
Some broadening was observed in the lowest frequency ^{13}CO band in the monophosphine complexes of 2,4-dimethyl-1,3-pentadiene and *trans*-1,3-pentadiene. In the latter case, this broadening was sufficient for two separate ^{13}CO peaks to be barely resolvable. Since the lowest frequency ^{13}CO peak of the tricarbonyl of both these dienes is also split, this suggests

Table IV. Observed Infrared Spectra of the Diene-Fe$(PF_3)(CO)_2$ Species in the Carbonyl Region (cm^{-1}) and Force Constants Calculated Assuming Equivalent Carbonyls (mdyn/Å)

						
	2028.1 s	2027.1 s	2027.9 s	2022.1 s	2024.4 s	2019.7 s
	1977.5 s	1976.2 s	1978.0 s	1971.1 s	1973.6 s	1964.6 s
	2014.2 w^a	2013.6 w^a	2013.3 w^a	2007.8 w^a	2010.0 w^a	2006.2 w^a
	1945.7 w^a	1944.2 w^{a,b}	1945.4 w^a	1939.9 w^a	1942.1 w^a	1938.7 w^{a,b}
K_2	16.20	16.18	16.20	16.10	16.14	16.03
$K_{2,2'}$	0.41	0.41	0.40	0.41	0.41	0.44

[a] ^{13}CO vibration. [b] Broadened or slightly split.

Table V. Observed Infrared Spectra of the Diene-Fe$(PF_3)_2(CO)$ Species in the Carbonyl Region (cm^{-1}) and Force Constants Calculated From the ^{12}CO Vibration (mdyn/Å)

						
^{12}CO	1997.0 s	1994.2 s	1997.4 s	1992.5 s	1992.9 s	1983.9 s
^{13}CO	1950.5 w	1947.6 w	1950.8 w	1946.5 w	1946.6 w	1938.6 w
K_2	16.10	16.06	16.11	16.03	16.04	15.89

that the splitting in the monophosphine may be due to a slight difference in K_2 and $K_{2'}$ rather than to the presence of additional isomers. This is further suggested by a close agreement of observed and predicted ^{13}CO isotope peaks for these complexes when C_s symmetry is assumed.

Force constant calculations were made for all monophosphines assuming both equivalent and nonequivalent carbonyls. For equivalent carbonyls the two ^{12}CO bands were used to calculate the two force constants K_2 and $K_{2,2'}$ and then predict the positions of the two ^{13}CO peaks. In the case of the nonequivalent carbonyls, two ^{12}CO bands and one ^{13}CO band can be used to calculate the three force constants K_1, K_2, and $K_{1,2}$ and then predict the remaining three ^{13}CO peaks. Assumption of equivalent CO groups gives the better result in every case. The force constants for these monophosphines are shown in Table IV. Recalculation of the force constants for (*trans*-1,3-pentadiene)Fe$(PF_3)(CO)_2$ taking the splitting of the low-frequency ^{13}CO band into account and assuming that the basal carbonyls are not equivalent suggests that K_2 and $K_{2'}$ do not differ by more than about 0.01 mdyn/Å.

For the diphosphine complexes, the carbonyl can occupy either the apical or one of the two basal positions. Infrared spectral data in the carbonyl region for these complexes are shown in Table V. None of the bands is split or appears excessively broad, suggesting that of the possible isomers, only one is present in amounts detectable by infrared spectroscopy. It is not possible to determine which isomer is preferred; however, by analogy with the butadiene system and as suggested by the preference of PF_3 for the apical site in the monophosphine complexes, the single carbonyl in the diphosphine is expected to occupy a basal site. Additional evidence supporting this assignment is provided by fluorine nmr and will be discussed in part B of this study.

The force constant K_2 can be determined from the ^{12}CO stretching vibration.[14] These values are listed in Table V.

Discussion

A series of dieneiron tricarbonyls is readily prepared by a photochemical reaction of dienes with $Fe(CO)_5$ or by a thermal reaction of dienes with $Fe_2(CO)_9$. Isomerization of the diene upon complexation sometimes occurs. Phosphorus trifluoride substitutes photochemically at 0° into the tricarbonyls to yield all possible compounds of the type (diene)Fe$(PF_3)_x(CO)_{3-x}$. These species were isolated by glpc and identified by a variety of techniques.

Isomers in the mono- and diphosphine species are possible for the square-based pyramidal structure that is assumed to be present. There are two basal positions and one apical position that could be occupied by carbonyl or phosphorus trifluoride groups yielding a maximum of two isomers for both the mono- and diphosphines if the basal sites are equivalent and three isomers if the basal sites are nonequivalent.

Infrared spectroscopy suggests that the methylbutadiene monophosphines resemble the analogous butadiene complex rather than the cyclohexadiene complex. In every case, the PF_3 group prefers the apical position, and only the isomer based on this preference can be detected by vibrational analysis. In the diphosphine complexes, again only one isomer appears to be present in detectable amounts. Although it is not possible to determine the structure of this preferred species, it seems reasonable to assume that the carbonyl occupies a basal site.

Force constants for all carbonyl complexes were calculated using an energy-factored force field.[14] In every case, the band assignments are exactly analogous to those found for the butadiene system.

Ligand–ligand competition has been used by Warren[2] to explain the result $K_1 > K_2$ for these complexes. There should be greater π bonding of the metal with the basal carbonyls than with the apical CO group because of less ligand–ligand competition for the π electrons available in the d_{xy} orbital.[2]

The preference of PF_3 for the apical site appears to be quite general for these complexes. Given the molecular dimensions of butadieneiron tricarbonyl[4] and the small size of the PF_3 ligand,[17] more than purely steric arguments seem required to account for the total absence of basal PF_3 in (butadiene)-Fe$(PF_3)(CO)_2$.[2] Since the apical site preference is least pronounced in the cyclohexadiene system where $K_1 = K_2$,[3] then an additional factor involved in determining isomer populations may be the relative π-bonding potential of PF_3 as compared to that of CO. Since PF_3 prefers the apical site with a poorer π-bonding potential, then for these systems, trifluorophosphine appears to be a weaker π-bonding ligand than carbon monoxide.[2]

Of particular interest is the effect of the methyl group on the stretching force constants in the tricarbonyl. There are three different substitution sites on the complexed butadiene ligand. The values of K_1 and K_2 for polymethyldiene complexes can be predicted by determining the effect of each type of methyl singly and then combining the results according to the number and position of groups in the polysubstituted complexes.

The effect of functional-group substitution on metal–olefin complexes has been reviewed.[18] It was concluded that the theory of σ–π bonding between metals and olefins was generally applicable to substituted olefin complexes. The main effect of any functional group was to modify the electronic properties of the olefin, thereby altering its σ–π bonding ability. Changes in the basic butadiene orbitals due to methyl

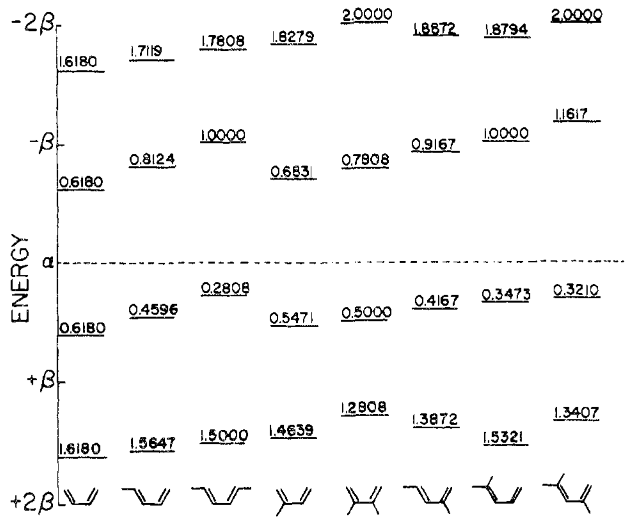


Figure 1. Huckel molecular orbital π energy level diagrams for butadiene and several methylbutadienes.

substitution can be determined using an extension of Huckel molecular orbital theory. A type of HMO calculation has been previously used to successfully predict the ease of formation of a variety of (diene)Fe(CO)$_3$ complexes.[19]

Simple HMO theory has been discussed in many texts and need not be developed here.[20] In the inductive model for an alkyl substituent,[20,21] the sole effect of the methyl is considered to be the creation of a small charge on the diene carbon to which it is directly attached. All of the resonance integral terms β are unaffected. The Coulomb integral terms α of the diene carbons with methyl substituents are expressed in units of a standard α_0 and β_0 by the equation

$$\alpha = \alpha_0 + h_x\beta_0 \tag{1}$$

The standard α_0 and β_0 will refer to the α and β terms associated with diene carbons within the π-electron system which are not attached to any group except hydrogen or other diene carbons. Since the methyl group is generally considered to be electron releasing, relative to hydrogen, the h_x term is negative. Suggested values for h_x range from -0.3 to -0.5.[20,21] The larger negative value of -0.5 was used in the calculations illustrated here. However, the use of any other value within the suggested range had no significant effect on the final results.

In terms of this model there is no theoretical reason to suppose that the position of substitution has any effect on the value of h_x. Thus, $h_x = -0.5$ was used for methyl groups located on both the central and terminal carbons of the diene. Likewise, substitution of two methyls on the same diene carbon was treated by doubling the negative charge, *i.e.*, $h_x = -1.0$. Inner and outer configurations on the terminal carbons were not distinguished.

Determinants for all the methyl-substituted butadienes were set up in the normal way,[20] and the roots of the resulting fourth degree polynomials were solved on a Data General Corp. Nova 1200. Assuming that the values of α_0 and β_0 are the same for each diene, the HMO energy level diagrams for these dienes are shown in Figure 1.

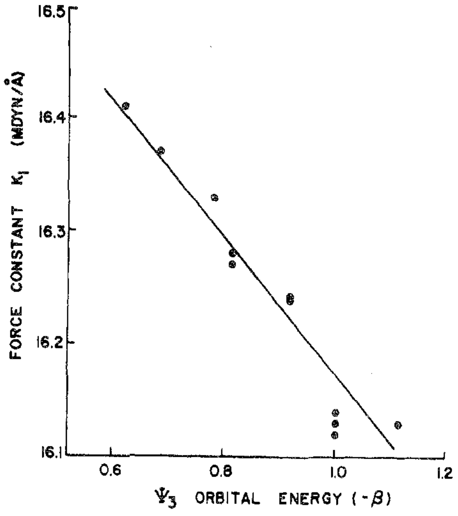


Figure 2. Plot of the HMO π energy of the ψ_3 orbitals *vs.* the CO stretching force constant K_1 for butadiene and several methylbutadienes.

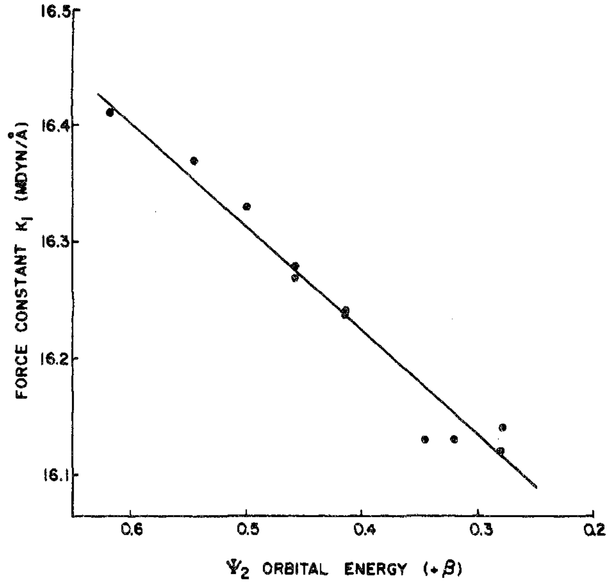


Figure 3. Plot of the HMO π energy of the ψ_2 orbitals *vs.* the CO stretching force constants K_1 for butadiene and several methylbutadienes.

The most important diene orbital for back-donation of metal electrons should be the lowest, unoccupied antibonding orbital ψ_3. Figure 1 shows that, in every case, the presence of a methyl group raises the level of the ψ_3 orbital, relative to that of butadiene. However, the position of substitution is quite important. Substitution on carbons 2 or 3 has less of an effect on the ψ_3 energy than substitution on carbons 1 or 4. The same effect is observed in the force constant K_1. For isopreneiron tricarbonyl K_1 is more similar to the analogous constant in the butadiene complex than K_1 for *trans*- or *cis*-1,3-pentadieneiron tricarbonyl.

A plot of K_1 *vs.* ψ_3 energies (Figure 2) has a correlation coefficient[16] of 0.94 indicating a very close relationship. A plot of K_1 *vs.* the energies of the highest occupied bonding orbital ψ_2 (Figure 3) also gives a very high correlation coefficient of 0.97.

The ψ_2 orbital is expected to be the most important diene orbital involved in σ bonding to the metal. However, since bonding in these complexes is synergic, the strength of the σ bond influences the strength of the π bond and *vice versa*. Therefore, the force constants which reflect the difference between bonding by CO and the diene are probably better considered as the result of changes in the overall σ–π bonding abilities of the ligands, not the result solely of variations in their π-bonding capacities. Thus both ψ_2 and ψ_3 are expected to be related to K_1.

Attempts to correlate K_2 with ψ_3 and ψ_2 energies resulted in correlation coefficients of only 0.83 and 0.78, respectively. A possible explanation for this can be found by considering

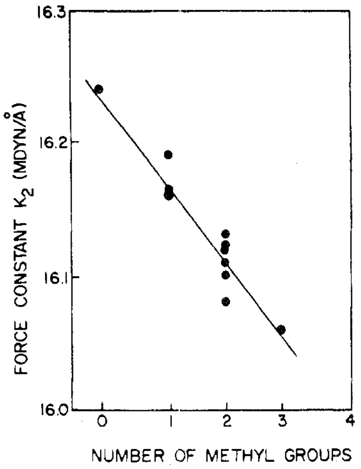


Figure 4. Plot of the number of methyl groups *vs.* the CO stretching force constant K_2 for butadiene and several methylbutadienes.

the two types of carbonyls in these complexes and the metal orbitals available for overlap with each.[2]

The apical carbonyl must compete with the diene for π electrons in each of the two metal orbitals to which it can π bond (d_{xz}, d_{yz}). The basal carbonyls share orbitals with the diene (d_{xz}, d_{yz}), but also bond to a metal orbital where the diene can not compete (d_{xy}). Therefore, it seems reasonable that, whereas the force constants for the apical carbonyl, K_1, should be directly related to the specific energies of the ψ_2 and ψ_3 orbitals and thus sensitive to the position of methyl substitution on the diene, the force constant for the basal carbonyl, K_2, may not be as directly related to the specific energies of the orbitals as it is to the overall effect of methyl substitution on the total charge on the metal. If the methyl group is electron releasing, a proportionate increase in charge should accumulate on the metal for each methyl group on the diene.[22] The total number of methyl substituents should, therefore, be related to the overall charge accumulation on the metal and therefore to K_2. A plot of the number of methyl substituents *vs.* K_2 (Figure 4) has a correlation coefficient of 0.95. These relationships suggest that the force constants are additive because each methyl contributes a constant amount of inductive charge to the diene, and the effect on the diene orbital energies depends on the position of substitution.

An additive effect on the ψ_2 and ψ_3 orbital energies by methyl substitution has been suggested by another phenomenon. The π–π^* transition in the uv region occurs at 217 nm for butadiene. Woodward[23] has shown that each alkyl group attached to the parent diene shifts the absorption 5 nm toward longer wavelengths. However, the shift is not particularly sensitive to the position of substitution, although small differences (about 0.5 nm) are observed for cis and trans isomers.

There is some disagreement over the band assignments in the electronic spectra of dienemetal carbonyl complexes[24,25] because of the presence of additional bands due to 3d–π^* transitions and possible shifts in the π–π^* transition upon complexation of the diene. Also, some of the observed bands are broad and do not vary much with change in substituent groups on the diene.[26] For these reasons, no attempt was made to correlate the electronic transitions observed in the uv spectra of these dieneiron tricarbonyl complexes with the K_1 and K_2 carbonyl stretching force constants.

Acknowledgment. The authors gratefully acknowledge the financial assistance of the NSF (Grant-36332X) during the course of this investigation.

Registry No. (1,3-Butadiene)Fe(CO)$_3$, 52610-59-0; (2,3-dimethyl-1,3-butadiene)Fe(CO)$_3$, 52993-10-9; (isoprene)Fe(CO)$_3$, 52993-11-0; (*trans,trans*-2,4-hexadiene)Fe(CO)$_3$, 52993-12-1; (*trans*-1,3-pentadiene)Fe(CO)$_3$, 32732-71-1; (*cis*-1,3-pentadiene)Fe(CO)$_3$, 12128-29-9; (2-methyl-*trans*-1,3-pentadiene)Fe(CO)$_3$, 52993-13-2; (2-methyl-*cis*-1,3-pentadiene)Fe(CO)$_3$, 52993-14-3; (4-methyl-1,3-pentadiene)Fe(CO)$_3$, 52993-15-4; (*cis,trans*-2,4-hexadiene)Fe(CO)$_3$, 52993-16-5; (2,4-dimethyl-1,3-pentadiene)Fe(CO)$_3$, 52993-17-6; (isoprene)Fe(PF$_3$)(CO)$_2$, 52950-80-8; (*trans*-1,3-pentadiene)Fe(PF$_3$)(CO)$_2$, 52950-81-9; (*cis*-1,3-pentadiene)Fe(PF$_3$)(CO)$_2$, 52993-18-7; (*trans,trans*-2,4-hexadiene)Fe(PF$_3$)(CO)$_2$, 52950-82-0; (2,3-dimethyl-1,3-butadiene)Fe(PF$_3$)(CO)$_2$, 52950-83-1; (2,4-dimethyl-1,3-pentadiene)Fe(PF$_3$)(CO)$_2$, 52950-84-2; (isoprene)Fe(PF$_3$)$_2$(CO), 52950-85-3; (*trans*-1,3-pentadiene)Fe(PF$_3$)$_2$(CO), 52950-86-4; (*cis*-1,3-pentadiene)Fe(PF$_3$)$_2$(CO), 52993-19-8; (*trans,trans*-2,4-hexadiene)Fe(PF$_3$)$_2$(CO), 52950-87-5; (2,3-dimethyl-1,3-butadiene)Fe(PF$_3$)$_2$(CO), 52950-88-6; (2,4-dimethyl-1,3-pentadiene)Fe(PF$_3$)$_2$(CO), 52950-89-7; Fe(CO)$_5$, 13463-40-6; Fe$_2$(CO)$_9$, 15321-51-4; 1,3-butadiene, 106-99-0; *trans*-1,3-pentadiene, 2004-70-8; *trans,trans*-2,4-hexadiene, 5194-51-4; isoprene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2-methyl-*trans*-1,3-pentadiene, 926-54-5; 4-methyl-1,3-pentadiene, 926-56-7; 2,4-dimethyl-1,3-pentadiene, 1000-86-8.

References and Notes

(1) (a) T. Kruck, *Angew. Chem., Int. Ed. Engl.*, **6**, 53 (1967); (b) R. J. Clark and M. A. Busch, *Accounts Chem. Res.*, **6**, 246 (1973).
(2) J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970).
(3) J. D. Warren, M. A. Busch, and R. J. Clark, *Inorg. Chem.*, **11**, 452 (1972).
(4) (a) O. S. Mills and G. Robinson, *Acta Crystallogr.*, **16**, 758 (1963); (b) F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Amer. Chem. Soc.*, **95**, 4522 (1973).
(5) R. B. King, "Organometallic Synthesis," Vol. I, Academic Press, New York, N. Y., 1965, p 93.
(6) R. L. Frank, R. D. Emmick, and R. S. Johnson, *J. Amer. Chem. Soc.*, **69**, 2313 (1947).
(7) G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).
(8) R. Ben-Shoshan and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 2231 (1967).
(9) IUPAC Commission on Molecular Structure and Spectroscopy, *Pure Appl. Chem.*, **1**, 582 (1961).
(10) (a) M. A. Haas and J. W. Wilson, *J. Chem. Soc. B*, 104 (1968); (b) J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, *J. Chem. Soc.*, 341 (1966).
(11) W. G. Dauben and M. E. Lorber, *Org. Mass Spectrom.*, **3**, 211 (1970).
(12) R. W. Kiser, M. A. Krassoi, and R. J. Clark, *J. Amer. Chem. Soc.*, **89**, 3653 (1967).
(13) J. C. Davis, Jr., *J. Amer. Chem. Soc.*, **88**, 1585 (1966).
(14) (a) E. B. Wilson, J. C. Decius, and T. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955; (b) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962), and other papers in this series.
(15) J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc. A*, 1208 (1968).
(16) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences," McGraw-Hill, New York, N. Y., 1969.
(17) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).
(18) R. Jones, *Chem. Rev.*, **68**, 785 (1968).
(19) B. J. Nicholson, *J. Amer. Chem. Soc.*, **88**, 5156 (1966).
(20) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.
(21) G. W. Wheland and L. Pauling, *J. Amer. Chem. Soc.*, **57**, 2086 (1935).
(22) D. A. Brown and H. Sloan, *J. Chem. Soc.*, 3849 (1962).
(23) R. B. Woodward, *J. Amer. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942).
(24) M. Cais and N. Maoz, *J. Organometal. Chem.*, **5**, 370 (1966).
(25) R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).
(26) (a) H. Alper and J. T. Edward, *J. Organometal. Chem.*, **14**, 411 (1968); (b) G. N. Schrauzer, *Inorg. Chem.*, **4**, 264 (1965).