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# Microwave Measurements of the Rotational Spectrum and Structure of (Butadiene)iron Tricarbonyl

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**Abstract:** The rotational spectra of 10 isotopomers of (butadiene)iron tricarbonyl were measured using a Flygare–Balle-type microwave spectrometer operating in the 5–17-GHz frequency range. The 30 measured rotational constants were used to determine 12 gas-phase structural parameters describing the *cis*-butadiene conformation and the locations and orientations of the butadiene and CO ligands relative to the iron atom. Kraitchman analyses of these microwave measurements, with single and multiple deuterium substitution, provide accurate data on the hydrogen atom coordinates in the complex. The terminal $CH_2$ groups of butadiene are found to be rotated by 28° out of the butadiene plane, and the $CH_2$ plane is folded away from the $C_1$–$C_2$ axis by 27° in a direction away from the iron atom. Least-squares fits to all rotational constants to determine structural parameters were also carried out, and the results are compared with coordinates from the Kraitchman method. Other structural parameters are compared with X-ray diffraction results on similar compounds. The four possible single-substitution $^{13}C$ isotopomers were observed in natural abundance samples. Samples for the two $D_1$, two $D_3$, and $D_4$ substitutions on terminal H atoms were synthesized. Proton NMR spectra were analyzed to obtain improved chemical shifts and coupling constants for this complex.

## Introduction

The structures of olefin–metal complexes have been of considerable interest due to their relation to the numerous heterogeneous catalysis reactions of alkenes on metal surfaces.[1] Both theoretical and experimental studies have focused on the electronic and structural changes of the olefin due to interactions with one or more metal atoms. Present theoretical calculations on isolated, small, rigid molecules give excellent results. However, the present calculations on the much more difficult case of olefin–transition metal complexes are much less reliable and accurate. This makes it important to have accurate gas-phase structural data to test and guide the calculations. Although X-ray diffraction methods have provided precise measurements of the heavy atom coordinates in numerous olefin–transition metal complexes,[2] there is evidence that these solid-state structures can suffer significant distortions from various lattice effects.[3] Moreover, these measurements often fail to reveal the location of the hydrogen atoms which are particularly sensitive to changes in the electronic structure of an olefin.

Microwave spectroscopy has provided the most accurate and precise structures currently available for a very large number of small molecules. However, one of the problems with molecules composed of more than 10–15 atoms is the large number of isotopomers which must be measured to completely determine the structure. This number can be greatly reduced, however, if the molecule contains a plane of symmetry or other symmetry elements. Microwave measurements using normal, deuterium-substituted, and carbon-13 isotopomers can provide accurate hydrogen and carbon atom coordinates for molecules in which these atoms are not too close to the center of mass or a principal axis. These gas-phase measurements are free of crystal packing distortions and can be compared directly with theoretical work.

The (butadiene)iron tricarbonyl complex (shown in Figure 1) is one of the earliest known π-bonded transition-metal complexes and was described by Reihlen and co-workers[4] in 1930. This complex did not attract nearly as much attention as ferrocene and other "sandwich"-type complexes since it was first thought to have a metalacycle-type structure with σ-bonding to the metal atom. The presently accepted π-bonded structure was proposed by Hallam and Pauson,[5] based primarily on the remarkable chemical stability of this complex. (Butadiene)iron tricarbonyl can be recovered intact from concentrated sulfuric acid and from boiling with maleic anhydride in benzene. This and other experimental results on reactions with ozone and lithium aluminum hydride supported the π-bonded structure. A large number of diene iron carbonyl complexes have been reviewed recently by Pettit and Emerson.[6]

The X-ray crystal structures of this[7] and related compounds[8] were used as the starting point for the present analysis. Hydrogen atom coordinates were not obtained in the X-ray work.[7] The microwave spectrum for the common isotopomer of (butadiene)iron tricarbonyl was reported earlier.[9] However, only a limited structural characterization was possible since this earlier study provided only three inertial constraints. In the present study, $^{13}C$ data is obtained for all possible substitution sites in addition to deuterium substitution in various combinations at four of the six possible sites. The lack of observable *b*-dipole transitions confirms an *a*,*c* plane of symmetry within the molecule. The total 33 measured rotational constants and the existence of an *a*,*c* plane of symmetry permit a molecular structure determination with very few assumed parameters obtained from other data.

## Experimental Section

Microwave spectra were measured using a Flygare–Balle-type spectrometer[10] equipped with a heated nozzle pulsed-beam source. The present spectrometer[11] employs solid-state microwave sources and 0.3-m-diameter mirrors with a single "antenna" for coupling signals in and out of the cavity. The solenoid pulse valve (General Valve 9-181) and sample reservoir were maintained at 30–40 °C to maintain sufficient sample vapor pressure. A factor of 2 improvement in signal-to-noise ratio

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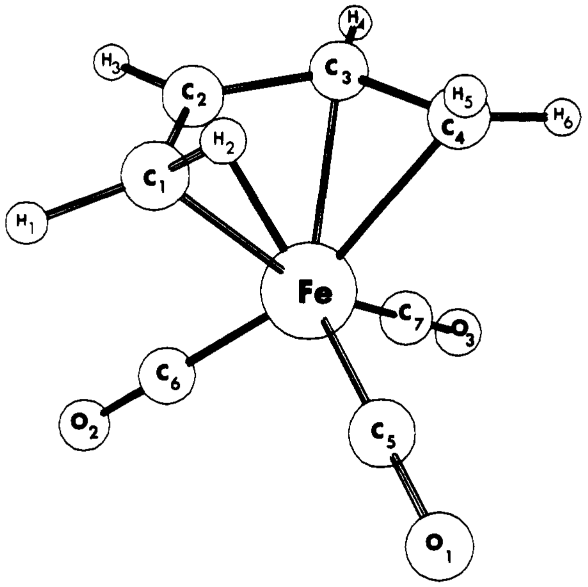

**Figure 1.** Structure of (butadiene)iron tricarbonyl determined from microwave measurements, with the numbering of atoms indicated.

was obtained using first-run neon (Airco) at 0.7 atm when compared with data for argon as the expansion gas.

Improved data acquisition rates for the $^{13}C$ isotopomers were obtained by pulsing the valve at 3 Hz and averaging 512-point fid signals. Some $^{13}C$ transitions were obtained with a 1:1 signal-to-noise ratio on a single beam pulse, and all reported transitions were obtained with a maximum 200–500 beam pulses. Nearly all reported transitions were significantly broadened by partially resolved hyperfine structure. This is most likely due to proton and $^{13}C$ spin–spin and spin–rotation interactions. Larger splitting and broadening effects were observed with the deuterated isotopomers, and this can most likely be attributed to deuterium quadrupole coupling effects. Due to the *a,c* mirror plane, 2% of the molecules have single $^{13}C$ substitution at $C_1$ and $C_2$ carbon sites in butadiene and $C_6$ and $C_7$ sites on the tricarbonyl portion. The $C_5$ carbonyl carbon is on the mirror plane, so only 1% substitution occurs at this site.

The deuterated isotopomers were synthesized from deuterated butadiene and $Fe(CO)_5$ as described by King.[12] Approximately 10 mL of liquid butadiene and 10 mL of $Fe(CO)_5$ (liquid) were placed in a 0.5-L lecture bottle and heated to 140 °C for 24 h. The CO was vented and the contents distilled out under vacuum. The excess butadiene and iron pentacarbonyl was pumped away at 30 °C. The $D_4$ butadiene was prepared from butadiene-*2,2,5,5-$d_4$* sulfone (Aldrich 32, 059-5) by passing the vapor through quartz helicies heated to 170 °C to pyrolyze the butadiene sulfone. The $SO_2$ was trapped by passing the butadiene–$SO_2$ gas mixture through a 30% aqueous KOH solution. The butadiene was dried using $P_2O_5$. The $D_1$ and $D_3$ butadiene samples were made by the base-catalyzed exchange of butadiene sulfone (Aldrich B8, 450-5) as described by Cope et al.[13] The quantities of $D_2O$ and butadiene sulfone were chosen to make the D/H ratio 1/4 for the $D_1$ isotopomer and 4/1 for the $D_3$ isotopomer. This would be expected to result in 32% $H_4$, 42% $D_1$, 21% $D_2$, and 5% $D_3$ for the $D_1$ preparation and corresponding $D_4$, $D_3$, $D_2$, and $D_1$ percentages for the $D_3$ preparation. The exchange takes place only for the butadiene terminal hydrogens (bonded to $C_2$ or $C_5$ of butadiene sulfone). $D_2$-substituted isotopomers were present in both preparations, but no attempt was made to analyze the resulting spectra since there are four possible distinctly different structural isomers with two deuterium substitutions and only two possible isomers for the $D_1$ and $D_3$ substitutions.

Both *a*- and *c*-dipole transitions were measured and are reported in Tables I, III, and V with experimental uncertainties of 1–4 kHz. Although not measured, weak *b*-dipole transitions are possible for isotopically substituted molecules where the substitution involves an atom not in the *a,c* plane.

**Data Analysis And Rotational Constants.** The data and the rotational constants for the normal isotopomer were published earlier.[9] The partially resolved hyperfine structure on the normal isotopomer is most likely due to proton spin–spin and spin–rotation interactions. The second largest data set was for the $D_4$ isotopomer. This is designated DDHH-DD, indicating deuterium substitution at $H_1$, $H_2$, $H_5$, and $H_6$ positions (See Figure 1). The results of least-squares fits to measured transitions

**Table I.** Measured Rotational Transition Frequencies for (Butadiene-$d_4$)iron Tricarbonyl (DDHHDD) and Measured Minus Calculated Frequencies[a]

| $J_{K_pK_o}$ | $J'_{K_p'K_o'}$ | measd | measd – calcd |
|---|---|---|---|
| $2_{12}$ | $3_{13}$ | 5368.262 | –0.0028 |
| $2_{02}$ | $3_{03}$ | 5383.335 | –0.0143 |
| $2_{11}$ | $3_{12}$ | 5494.338 | –0.0081 |
| $2_{02}$ | $3_{12}$ | 5649.664 | –0.0139 |
| $2_{11}$ | $3_{21}$ | 5668.786 | –0.0022 |
| $2_{12}$ | $3_{22}$ | 5720.079 | 0.0172 |
| $2_{20}$ | $3_{30}$ | 5790.435 | –0.0094 |
| $2_{21}$ | $3_{31}$ | 5803.895 | –0.0124 |
| $3_{13}$ | $4_{14}$ | 7144.452 | 0.0022 |
| $3_{03}$ | $4_{04}$ | 7150.225 | 0.0020 |
| $3_{22}$ | $4_{23}$ | 7243.688 | –0.0051 |
| $3_{31}$ | $4_{32}$ | 7286.710 | 0.0025 |
| $3_{12}$ | $4_{13}$ | 7289.958 | –0.0182 |
| $3_{21}$ | $4_{22}$ | 7351.535 | –0.0127 |
| $3_{12}$ | $4_{22}$ | 7525.982 | –0.0069 |
| $3_{03}$ | $4_{13}$ | 7556.314 | 0.0095 |
| $3_{21}$ | $4_{31}$ | 7601.693 | –0.0130 |
| $3_{22}$ | $4_{32}$ | 7645.865 | 0.0027 |
| $3_{30}$ | $4_{40}$ | 7748.936 | 0.0075 |
| $3_{31}$ | $4_{41}$ | 7753.454 | 0.0073 |
| $4_{14}$ | $5_{15}$ | 8917.205 | 0.0025 |
| $4_{04}$ | $5_{05}$ | 8918.929 | 0.0037 |
| $4_{23}$ | $5_{24}$ | 9031.921 | 0.0008 |
| $4_{13}$ | $5_{14}$ | 9060.779 | 0.0082 |
| $4_{32}$ | $5_{33}$ | 9101.770 | –0.0055 |
| $4_{41}$ | $5_{42}$ | 9177.115 | 0.0101 |
| $4_{22}$ | $5_{23}$ | 9176.419 | –0.0036 |
| $4_{31}$ | $5_{32}$ | 9178.073 | 0.0048 |
| $4_{13}$ | $5_{23}$ | 9412.447 | 0.0122 |
| $4_{22}$ | $5_{32}$ | 9428.228 | 0.0014 |
| $4_{23}$ | $5_{33}$ | 9503.941 | –0.0030 |
| $4_{31}$ | $5_{41}$ | 9559.740 | –0.0102 |
| $4_{32}$ | $5_{42}$ | 9583.843 | –0.0011 |
| $4_{41}$ | $5_{51}$ | 9706.320 | –0.0003 |
| $5_{15}$ | $6_{16}$ | 10 688.602 | 0.0041 |
| $5_{05}$ | $6_{06}$ | 10 689.048 | –0.0024 |
| $5_{24}$ | $6_{25}$ | 10 811.437 | 0.0037 |
| $5_{14}$ | $6_{15}$ | 10 823.891 | 0.0010 |
| $5_{33}$ | $6_{34}$ | 10 905.772 | –0.0122 |
| $5_{41}$ | $6_{42}$ | 10 983.579 | –0.0025 |
| $5_{32}$ | $6_{33}$ | 11 031.461 | 0.0007 |
| $6_{16}$ | $7_{17}$ | 12 459.567 | 0.0014 |
| $6_{06}$ | $7_{07}$ | 12 459.675 | –0.0009 |
| $6_{25}$ | $7_{26}$ | 12 585.703 | 0.0058 |
| $6_{15}$ | $7_{16}$ | 12 589.951 | 0.0077 |
| $6_{34}$ | $7_{35}$ | 12 697.723 | 0.0104 |
| $6_{24}$ | $7_{25}$ | 12 740.675 | –0.0127 |
| $6_{43}$ | $7_{44}$ | 12 762.999 | 0.0055 |
| $7_{17}$ | $8_{18}$ | 14 230.425 | 0.0061 |
| $7_{07}$ | $8_{08}$ | 14 230.456 | 0.0115 |
| $7_{26}$ | $8_{27}$ | 14 357.565 | –0.0089 |
| $8_{08}$ | $9_{09}$ | 16 001.249 | –0.0001 |
| $9_{09}$ | $10_{010}$ | 17 772.052 | –0.0091 |

[a] The calculated frequencies were obtained from a least-squares fit to measured frequencies using parameters listed in Table II.

**Table II.** Rotational and Centrifugal Distortion Constants Obtained from the Least-Squares Fit to 53 Transitions in (Butadiene-$d_4$)iron Tricarbonyl (DDHHDD)

| parameter | value[a] | units |
|---|---|---|
| $A$ | 977.208(2) | MHz |
| $B$ | 929.481(2) | MHz |
| $C$ | 885.430(1) | MHz |
| $\Delta_J$ | 0.11(2) | kHz |
| $\Delta_{JK}$ | –0.02(11) | kHz |
| $\Delta_K$ | –0.07(12) | kHz |
| $\delta_J$ | 0.046(14) | kHz |
| $\delta_K$ | –0.32(7) | kHz |

[a] The listed errors are two standard deviations. The standard deviation for the fit was 9 kHz.

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**Table III.** Measured Transition Frequencies for Single and Triple Deuterium Substitutions in (Butadiene)iron Tricarbonyl[a]

| $J_{K_pK_o} \rightarrow J'_{K_p'K_o'}$ | *C* (DHHHHH) | *D* (HDHHHH) | *B* (HDHHDD) | *A* (DHHHDD) |
|---|---|---|---|---|
| $3_{13} \rightarrow 4_{15}$ | 7407.795 | 7415.713 | 7235.050 | 7226.560 |
| $3_{03} \rightarrow 4_{04}$ | 7413.541 | 7426.952 | 7244.851 | 7230.788 |
| $3_{22} \rightarrow 4_{23}$ | 7482.467 | 7470.043 | | 7324.514 |
| $3_{31} \rightarrow 4_{32}$ | | 7485.409 | 7337.750 | 7370.111 |
| $3_{30} \rightarrow 4_{31}$ | | | | |
| $3_{12} \rightarrow 4_{13}$ | | 7507.788 | | 7365.163 |
| $3_{21} \rightarrow 4_{22}$ | | 7518.045 | | 7433.457 |
| $3_{12} \rightarrow 4_{22}$ | 7704.375 | 7684.908 | | |
| $3_{03} \rightarrow 4_{13}$ | | | | |
| $3_{13} \rightarrow 4_{23}$ | | | | |
| $3_{21} \rightarrow 4_{31}$ | 7776.935 | 7810.186 | | |
| $3_{22} \rightarrow 4_{32}$ | | 7832.582 | | |
| $3_{30} \rightarrow 4_{40}$ | 7901.428 | 7956.663 | | |
| $3_{31} \rightarrow 4_{41}$ | 7904.312 | 7957.606 | | |
| $4_{14} \rightarrow 5_{15}$ | 9249.765 | 9263.070 | 9033.915 | 9019.970 |
| $4_{04} \rightarrow 5_{05}$ | 9251.678 | 9268.807 | 9037.900 | 9021.097 |
| $4_{23} \rightarrow 5_{24}$ | | 9329.662 | 9125.696 | |
| $4_{13} \rightarrow 5_{14}$ | | 9366.326 | 9164.643 | 9154.035 |
| $4_{32} \rightarrow 5_{33}$ | 9387.095 | 9357.078 | 9170.859 | |
| $4_{41} \rightarrow 5_{42}$ | | | | |
| $4_{40} \rightarrow 5_{41}$ | | | | |
| $4_{31} \rightarrow 5_{32}$ | | | 9211.142 | |
| $4_{22} \rightarrow 5_{23}$ | | 9403.591 | 9235.041 | 9273.415 |
| $4_{13} \rightarrow 5_{23}$ | 9269.390 | 9580.712 | | |
| $4_{04} \rightarrow 5_{14}$ | | | | |
| $4_{22} \rightarrow 5_{32}$ | 9654.082 | 9668.870 | 9505.815 | |
| $4_{14} \rightarrow 5_{24}$ | | | | |
| $4_{23} \rightarrow 5_{33}$ | | 9719.613 | 9574.918 | |
| $4_{31} \rightarrow 5_{41}$ | 9771.694 | | 9669.265 | |
| $4_{32} \rightarrow 5_{42}$ | 9787.894 | 9830.373 | 9681.746 | |
| $4_{40} \rightarrow 5_{50}$ | 9892.302 | | 9821.315 | |
| $4_{41} \rightarrow 5_{51}$ | 9892.994 | | 9821.700 | |
| $5_{15} \rightarrow 6_{16}$ | 11 090.472 | 11 108.792 | 10 831.012 | 10 812.307 |
| $5_{05} \rightarrow 6_{06}$ | 11 091.034 | 11 111.293 | 10 832.439 | 10 812.571 |
| $5_{24} \rightarrow 6_{25}$ | 11 185.355 | 11 184.954 | 10 933.175 | 10 930.429 |
| $5_{14} \rightarrow 6_{15}$ | | 11 213.488 | 10 957.447 | |
| $5_{33} \rightarrow 6_{34}$ | | | 10 998.417 | 11 025.852 |
| $5_{23} \rightarrow 6_{24}$ | 11 310.611 | 11 281.246 | 11 067.470 | 11 081.849 |
| $5_{32} \rightarrow 6_{33}$ | 11 343.755 | | 11 076.574 | 11 385.863 |
| $5_{32} \rightarrow 6_{42}$ | | | | 11 442.137 |
| $5_{33} \rightarrow 6_{43}$ | | | | 11 502.384 |
| $5_{41} \rightarrow 6_{51}$ | 11 767.210 | | | 11 578.554 |
| $5_{42} \rightarrow 6_{52}$ | | | | 11 589.691 |
| $5_{50} \rightarrow 6_{60}$ | | | 11 800.262 | 11 702.427 |
| $5_{51} \rightarrow 6_{61}$ | | | | 11 702.817 |
| $6_{06} \rightarrow 7_{07}$ | | 12 954.633 | | |

[a] Frequencies in MHz. Typical values for experimental uncertainties of line positions are 0.005 MHz.

**Table IV.** Rotational and Distortion Constants Obtained from Least-Squares Fits to Multiple Deuterium Substitution (Butadiene)iron Tricarbonyl Data Listed in Table III[a]

| parameter | DDHHDD | DHHHHH | HDHHHH | HDHHDD | DHHHDD |
|---|---|---|---|---|---|
| *A* (MHz) | 977.209(2) | 994.857(2) | 1003.106(2) | 989.396(4) | 980.095(6) |
| *B* (MHz) | 929.482(2) | 953.270(2) | 946.693(3) | 932.192(4) | 939.458(2) |
| *C* (MHz) | 885.430(2) | 920.074(2) | 922.098(2) | 897.968(2) | 895.995(2) |
| $\Delta_J$ (kHz) | 0.11(2) | 0.08(3) | 0.06(3) | 0.05(4) | 0.03(3) |
| $\Delta_{JK}$ (kHz) | −0.02(6) | 0.016[b] | 0.016[b] | 0.2(2) | 0.1(1) |
| $\Delta_K$ (kHz) | −0.07(7) | 0.010[b] | −0.010[b] | −0.1(2) | −0.11(8) |
| $\delta_J$ (kHz) | 0.05(1) | 0.002[b] | 0.030(2) | 0.02(2) | −0.04(2) |
| $\delta_K$ (kHz) | −0.3(1) | −0.2(1) | −0.2(2) | −0.4(2) | −0.33(8) |

[a] Listed uncertainties are $2\sigma$. [b] These parameters were fixed at values obtained for the normal isotopomer.[9]

using a Watson-type *A*-reduced Hamiltonian in the $I^r$ representation[14] are shown in Table I. Fifty transitions were fit with a standard deviation of 9 kHz to obtain the rotational constants and distortion parameters listed in Table II. These spectra exhibited line broadening due to unresolved deuterium hyperfine structure. Although the resulting experimental errors are substantially larger than those obtained for the normal $H_6$ isotopomer,[9] the distortion parameters are in reasonable agreement with the earlier work.

Smaller data sets were obtained for the $D_1$ and $D_3$ partially deuterated isotopomers. Resolved and partially resolved hyperfine splitting was observed on many transitions as with $D_4$ data, and we attribute this primarily to deuterium hyperfine interactions. All measured lines for these partially deuterated samples, which were used in the least-squares fits, are listed in Table III. Standard deviations for these fits were less than 10 kHz, and the resulting rotational constants and distortion parameters are listed in Table IV. The isotopomers are designated by the positions of deuterium substitution, with the hydrogen positions numbered 1–6, as indicated in Figure 1. For example, HDHHHH represents a single deuterium substitution at hydrogen position $H_2$ and is equivalent to HHHHDH due to the *a,c* mirror plane of the complex.

The measured $^{13}C$ isotopomer transition frequencies are listed in Table V. $C_1$* indicates a single $^{13}C$ substitution at carbon 1, the carbon atom numbering given in Figure 1. The rotational constants and distortion parameters for the $^{13}C$ data are given in Table VI. The consistency and

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**Table V.** Measured Transition Frequencies for Single $^{13}C$ Substitutions in (Butadiene)iron Tricarbonyl[a]

| $J_{K_pK_o} \to J'_{K_p'K_o'}$ | $C_1^*$ | $C_2^*$ | $C_5^*$ | $C_6^*$ |
|---|---|---|---|---|
| $3_{13} \to 4_{14}$ | 7447.803 | 7464.537 | 7499.455 | 7469.191 |
| $3_{03} \to 4_{04}$ | 7456.730 | 7474.572 | 7509.073 | 7477.418 |
| $3_{22} \to 4_{23}$ | 7507.859 | 7513.960 | 7540.603 | 7528.650 |
| $3_{12} \to 4_{13}$ | 7545.859 |  | 7570.055 | 7565.622 |
| $3_{30} \to 4_{31}$ |  | 7533.934 |  |  |
| $3_{31} \to 4_{22}$ | 7565.203 | 7557.901 | 7575.656 | 7586.417 |
| $3_{12} \to 4_{22}$ | 7716.867 | 7707.471 | 7712.671 | 7731.273 |
| $3_{03} \to 4_{13}$ | 7720.698 |  |  |  |
| $3_{21} \to 4_{31}$ |  |  | 7818.533 |  |
| $3_{22} \to 4_{32}$ |  |  | 7834.964 |  |
| $3_{30} \to 4_{40}$ | 7954.750 | 7950.590 | 7937.706 | 7956.019 |
| $3_{31} \to 4_{41}$ | 7956.187 | 7951.473 | 7938.333 | 7957.534 |
| $4_{14} \to 5_{15}$ | 9302.110 | 9324.661 | 9369.461 | 9328.850 |
| $4_{04} \to 5_{05}$ | 9306.015 | 9329.714 |  | 9332.535 |
| $4_{13} \to 5_{14}$ |  |  | 9449.656 | 9432.233 |
| $4_{23} \to 5_{24}$ | 9374.592 | 9385.188 |  |  |
| $4_{32} \to 5_{33}$ |  |  |  | 9434.823 |
| $4_{22} \to 5_{23}$ |  |  | 9475.016 | 9485.036 |
| $4_{13} \to 5_{23}$ |  |  | 9617.631 |  |
| $4_{22} \to 5_{32}$ |  | 9689.797 |  |  |
| $4_{23} \to 5_{33}$ |  |  |  | 9759.346 |
| $4_{31} \to 5_{41}$ | 9831.617 | 9829.213 |  | 9838.036 |
| $4_{32} \to 5_{42}$ | 9840.423 |  |  |  |
| $4_{40} \to 5_{50}$ |  |  |  | 9960.535 |
| $4_{41} \to 5_{41}$ |  |  | 9936.429 | 9960.799 |
| $5_{15} \to 6_{16}$ |  | 11 183.319 | 11 238.000 | 11 187.071 |
| $5_{05} \to 6_{06}$ | 11 156.377 | 11 185.497 | 11 240.539 | 11 188.343 |

[a] Frequencies in MHz. Typical values for experimental uncertainties of line positions are 0.005 MHz. $C_1^*$ indicates $^{13}C$ substitution at $C_1$, etc.

**Table VI.** Rotational and Distortion Constants Obtained from Least-Squares Fits to Single $^{13}C$-Substituted (Butadiene)iron Tricarbonyl Data Listed in Table V[a]

| parameter | $C_1^*$ | $C_2^*$ | $C_5^*$ | $C_6^*$ |
|---|---|---|---|---|
| $A$ (MHz) | 1002.124(2) | 1001.473(2) | 999.188(2) | 1001.929(2) |
| $B$ (MHz) | 952.765(1) | 951.010(1) | 952.378(2) | 955.267(2) |
| $C$ (MHz) | 925.850 | 928.660(1) | 933.684(1) | 928.615(1) |
| $\Delta_J$ (kHz) | 0.04(2) | 0.05(2) | 0.10(1) | 0.12(1) |
| $\Delta_{JK}$ (kHz) | 0.15(8) | 0.18(5) | 0.10(4) | 0.04(5) |
| $\delta_J$ (kHz) | −0.01(1) | −0.01(1) | 0.03(1) | 0.05(1) |
| $\delta_k$ (KhZ) | −0.32(8) | −0.3(1) | −0.4(2) | −0.2(1) |

[a] Listed uncertainties are $2\sigma$.

precision of the results for this data are better than that for the deuterium data, due to smaller hyperfine splitting effects. Experimental uncertainties for the rotational constants are 2 kHz or less ($2\sigma$).

**Table VII.** Results of the Least-Squares Fit To Determine 12 Structural Parameters for (Butadiene)iron Tricarbonyl[a]

| isotopomer | parameter | exptl value | calcd | exptl − calcd |
|---|---|---|---|---|
| normal (HHHHHH) | $A$ | 1005.420 | 1005.434 | −0.014 |
|  | $B$ | 958.041 | 958.047 | −0.006 |
|  | $C$ | 933.687 | 933.684 | 0.002 |
| (DHHHHH) | $A$ | 994.857 | 994.836 | 0.021 |
|  | $B$ | 953.270 | 953.269 | 0.002 |
|  | $C$ | 920.074 | 920.090 | −0.016 |
| (HDHHHH) | $A$ | 1003.106 | 1003.160 | −0.054 |
|  | $B$ | 946.693 | 946.699 | −0.005 |
|  | $C$ | 922.098 | 922.079 | 0.020 |
| (HDHHDD) | $A$ | 989.396 | 989.389 | 0.007 |
|  | $B$ | 932.192 | 932.210 | −0.019 |
|  | $C$ | 897.968 | 897.965 | 0.003 |
| (DHHHDD) | $A$ | 980.095 | 980.092 | 0.003 |
|  | $B$ | 939.458 | 939.426 | 0.032 |
|  | $C$ | 895.995 | 896.016 | −0.020 |
| (DDHHDD) | $A$ | 977.209 | 977.185 | 0.024 |
|  | $B$ | 929.482 | 929.452 | 0.030 |
|  | $C$ | 885.430 | 885.458 | −0.027 |
| $C_1^*$ | $A$ | 1002.124 | 1002.100 | 0.024 |
|  | $B$ | 952.765 | 952.775 | −0.010 |
|  | $C$ | 925.850 | 925.843 | 0.007 |
| $C_2^*$ | $A$ | 1001.473 | 1001.464 | 0.009 |
|  | $B$ | 951.010 | 951.022 | −0.011 |
|  | $C$ | 928.660 | 928.652 | 0.008 |
| $C_5^*$ | $A$ | 999.188 | 999.192 | −0.004 |
|  | $B$ | 952.378 | 952.377 | 0.001 |
|  | $C$ | 933.684 | 933.684 | −0.000 |
| $C_6^*$ | $A$ | 1001.929 | 1001.942 | −0.013 |
|  | $B$ | 955.267 | 955.280 | −0.013 |
|  | $C$ | 928.615 | 928.595 | 0.020 |

[a] The standard deviation for the fit was 24 kHz. The resulting parameters are listed in Table VIII. Values in MHz.

**Table VIII.** Structural Parameters Determined by Fitting the Experimental Rotational Constants given in Table VII[a]

| adjustable parameters | value |
|---|---|
| $\phi$ | 28.1(3)° |
| $\gamma$ | 26.6(1.0)° |
| $\theta$ | 118.3(5)° |
| $r(C_1–C_2)$ | 1.385(18) Å |
| $r(C_2–C_3)$ | 1.421(13) Å |
| $r(Fe–C_1)$ | 2.13(2) Å |
| $r(Fe–C_2)$ | 2.09(2) Å |
| $r(Fe–C_5)$ | 1.77(2) Å |
| $r(Fe–C_6)$ | 1.783(13) Å |
| $\alpha$ | 82.5(9)° |
| $\beta$ | 52.1(4)° |
| $\chi$ | 113.4(8)° |
| **fixed parameters** | **value** |
| $r(C_1–H_1)$ | 1.087 |
| $r(C_1–H_2)$ | 1.087 |
| $r(C_2–H_3)$ | 1.090 |
| $r(C_5–O_1)$ | 1.149 |
| $r(C_6–O_2)$ | 1.149 |
| $\angle H_1–C_1–H_2$ | 117.0 |
| $\angle H_3–C_2–C_3$ | 120.0 |
| $\angle Fe–C_5–O_1$ | 180.0 |
| $\angle Fe–C_6–O_2$ | 180.0 |

[a] Indicated uncertainties are two standard deviations ($2\sigma$).

**Structure Determination.** The (butadiene)iron tricarbonyl structural parameters were determined by using a least-squares procedure to fit the 30 available rotational constants for all of the measured isotopomers and by using the Kraitchman equations, as described below. In principle, a sufficient number of parameters are available to determine the 21 independent structural parameters with a least-squares fit, but this is not practical due to convergence problems. In the present work, the most significant, and least well known, structural parameters were optimized, while a few of the parameters, such as C–O and C–H bond lengths, were fixed at values determined previously. As many as 16 variable parameters were tested in various combinations in the structure fitting program. The most satisfactory results were obtained using 12 parameters with a resulting 24-kHz standard deviation of the calculated rotational constants from experimental values. The results are shown in Tables VII and VIII. In further tests, the terminal hydrogen parameters $r(C_1–H_1)$ and $\angle H_1–C_1–H_2$, the carbonyl angles $\angle Fe–C_5–O_1$ and $\angle Fe–C_6–O_2$, or the carbonyl bond lengths $r(C_5–O_1)$ and $r(C_6–O_2)$ were included as variable parameters in various runs of the fitting procedure, but the fit was not significantly improved and the optimized values for these parameters fell within error limits of the previously determined fixed values (Table VIII). The C–O bond length was fixed at 1.149 Å, an average value from X-ray data[2] on metal carbonyls. The fixed parameters describing the H–C bond lengths and related angles were obtained from the gas-phase microwave work of Caminati, Grassi, and Bauder[15] on free *cis*-butadiene. A slightly better fit was obtained with $\angle H_1–C_1–H_2 = 116°$, but the difference between this fit and the fixed value fit was not significant. Although metal–carbon–oxygen angles in X-ray work often differ from 180° by a few degrees, the 180° value provided the best fit to our gas-phase data.

The angle $\phi$ is the rotation of the $CH_2$ plane about the $C_1–C_2$ bond, in a direction to make this plane nearly perpendicular to the Fe–$C_1$ bond. When $\gamma = 0$, this could be described as a dihedral angle between $H_2–C_1$ and $H_3–C_2$ bonds. The angle $\gamma$ measures a folding of the $CH_2$ plane away from a continuation of the $C_2–C_1$ bond axis and away from the Fe atom. The angle $\alpha$ is the angle between the Fe–$C_5$ bond direction and the $z$ axis. The $z$ axis passes through the Fe atom and is perpendicular to the butadiene plane (as defined by the four carbon atoms). The angle $\beta$ is the angle between the Fe–$C_6$ or the Fe–$C_7$ bond direction and the

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[15] Caminati, W.; Grassi, G.; Bauder, A. *Chem. Phys. Lett.* **1988**, *148*, 13.

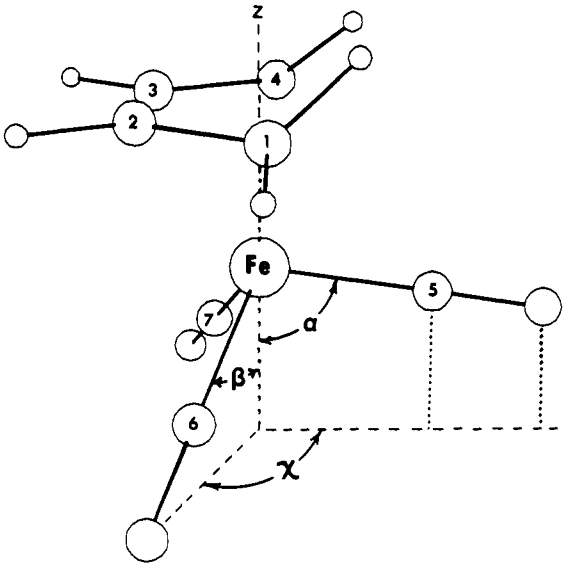

**Figure 2.** Diagram of (butadiene)iron tricarbonyl showing the angles α, β, and χ. The carbon atoms are numbered. The $z$ axis is perpendicular to the butadiene $C_1$–$C_2$–$C_3$–$C_4$ plane. The $x,z$ plane contains the Fe and $C_5$ atoms.

$z$ axis. The parameters α, β, and χ, describing the $Fe(CO)_3$ structure, are shown in Figure 2. The planes containing the angles α and β were initially placed at 120° away from each other around the $z$ axis, but better fits were obtained by making the angle between the plane containing α and the plane containing β a variable (denoted by χ). The best-fit value of $\chi = 113°$ is significantly smaller than 120°, indicating the influence of butadiene on the iron–carbonyl bonding.

**Kraitchman Analysis.** A Kraitchman analysis was carried out using our new experimental rotational constants to obtain coordinates for the substituted atoms. The equations for single isotopic substitution on a nonplanar asymmetric top[16] were used for the singly deuterated and single $^{13}C$ rotational constants. In the analysis of the $D_3$ triple-deuterium-substitution isotopomer data, the $D_4$ isotopomer DDHHDD was used as the reference compound, with single substitutions of hydrogen for deuterium for the Kraitchman analysis. This provided a second set of data for the terminal protons. The analyses yielded the absolute values of the $a$, $b$, and $c$ principal axis system coordinates for each of the labeled atoms relative to the center of mass system of the normal (butadiene)iron tricarbonyl ($BuFe(CO)_3$) isotopomer. Since the complex contains a plane of symmetry (bisecting the butadiene and containing the unique carbonyl group $C_5O_1$), nearly enough structural parameters such as bond lengths and angles could be obtained to describe the overall geometry of the $BuFe(CO)_3$ complex from the Kraitchman analysis. A fairly detailed description of the butadiene fragment was obtained since coordinates for all but two of the atoms ($H_3$ and $H_4$) could be calculated. For the least-squares fit analysis (above), the bond lengths for the terminal protons $H_1$–$C_1$ and $H_2$–$C_1$ were constrained to be equal. In the Kraitchman analysis, the $H_1$–$C_1$ bond was found to be 0.007 Å longer than the $H_2$–$C_1$ bond.

The results of the Kraitchman analysis are listed in Table IX. Only the first four bond lengths and the first four angles were determined entirely from the Kraitchman analysis data. Other parameters required the Fe coordinates in the principal axis system from fit results as discussed below.

The dihedral angles between $H_1$–$C_1$–$C_2$–$H_3$ and $H_2$–$C_1$–$C_2$–$H_3$ atoms were calculated by fixing the $H_3$ position in the carbon skeleton plane at 120° to the $C_2$–$C_3$ bond with a bond length of 1.090 Å. These parameters also show differences in the terminal hydrogen coordinates as discussed above.

The structure of the $Fe(CO)_3$ portion of the molecule can be evaluated using the Kraitchman analysis as well. To accomplish this, the location of the Fe atom relative to the center of mass for the molecule must be calculated using the fit results since the Fe atom was not isotopically labeled. The coordinates in the $(a,b,c)$ frame for Fe obtained from the structure fit were used in the Kraitchman analysis. The Fe atom is so close to the center-of-mass that the uncertainties from the fit results should not introduce any significant additional error into these Kraitchman-derived coordinates. Additional information on the terminal hydrogen positions can be obtained from a Kraitchman analysis using the $D_4$ isotopomer as the reference structure and the $D_3$ isotopomer for the single hydrogen substitution. We cannot determine the $C_1$–$H_1$ or the $C_1$–$H_2$ interatomic distances from these data sets, however. To calculate these distances we must assume a location for the Fe atom in the $D_4$ $(a,b,c)$ coordinate system. The iron coordinates from the results of the $D_4$ isotopomer structure fit were used in a similar manner as for the normal isotopic Kraitchman analysis. Values for Fe–$H_1$ and Fe–$H_2$ distances were 2.8304 and 2.6623 Å, respectively. When compared to values in Table IX, the agreement between these distances in the $D_4$ and $H_4$ analyses is remarkably good. Overall, the results from the Kraitch-

**Table IX.** Comparison of Interatomic Distances and Selected Angles Derived from the Kraitchman Analysis with the Fe Coordinates from the Structural Fit and Comparable Parameters Determined Entirely from the Structural Fit

| | Kraitchman | structural fit |
|---|---|---|
| | Bond Lengths (Å) | |
| H1–C1[a] | 1.0958(2) | 1.087 |
| H2–C1[a] | 1.089(5) | 1.087 |
| C1–C2[a] | 1.385(7) | 1.385 |
| C2–C3[a] | 1.409(1) | 1.421 |
| C1–Fe | 2.1270(3) | 2.127 |
| C2–Fe | 2.0870(2) | 2.088 |
| C3–Fe | 2.0870(2) | 2.088 |
| H1–Fe | 2.8230(1) | 2.815 |
| H2–Fe | 2.6511(7) | 2.650 |
| Fe–C5 | 1.7706(0) | 1.771 |
| Fe–C6 | 1.7824(9) | 1.783 |
| Fe–C7 | 1.7824(9) | 1.783 |
| | Angles (deg) | |
| H1–C1–H2[a] | 120.8(3) | 117.0 |
| H1–C1–C2[a] | 112.1(4) | 117.9 |
| H2–C1–C2[a] | 118.6(2) | 117.9 |
| C1–C2–C3[a] | 118.4(2) | 118.2 |
| $z$ axis–Fe–C5 | 81.5(5) | 82.4 |
| $z$ axis–Fe–C6 | 52.2(1) | 52.0 |
| $z$ axis–H1–O2 | 20.5(2) | 19.6 |
| $z$ axis–Fe–O3 | 52.2(2) | 52.0 |
| $x,z$ plane–$z$ axis–O2 | 113.8(2) | 113.3 |
| $x,z$ plane–$z$ axis–O3 | 113.8(2) | 113.3 |
| | Dihedral Angles (deg) | |
| H1–C1–C2–H3 | 11.3(3) | 12.8 |
| H2–C1–C2–H3 | 136.9(2) | 136.5 |

[a] For these parameters, the Kraitchman column values were determined entirely from the Kraitchman analysis; other parameters required data from the fit results or other measurements.

**Table X.** Cartesian Coordinates (in Å) of the Atoms in (Butadiene)iron Tricarbonyl as Determined from the Kraitchman Analysis with the Fe Coordinates from the Least-Squares Fit[a]

| atom | $X$ | $Y$ | $Z$ |
|---|---|---|---|
| $H_1$ | 0.011(5) | 2.434(65) | −0.199(8) |
| $H_2$ | 0.912(8) | 0.995(4) | 0.653(5) |
| $H_3$ | −2.04 | 1.25 | 0.000 |
| $C_1$ | 0.121(8) | 1.362(6) | 0.000 |
| $C_2$ | −1.098(13) | 0.705(8) | 0.000 |
| $C_3$ | −1.098(13) | −0.705(8) | 0.000 |
| $C_4$ | 0.121(8) | −1.362(6) | 0.000 |
| $H_4$ | −2.04 | −1.25 | 0.000 |
| $H_5$ | 0.912(8) | −0.995(4) | 0.653(5) |
| $H_6$ | 0.011(5) | −2.434(65) | −0.199(8) |
| Fe | 0.000 | 0.000 | −1.629(3) |
| $C_5$ | 1.751(62) | 0.000 | −1.891(10) |
| $C_6$ | −0.568(7) | −1.288(29) | −2.723(16) |
| $C_7$ | −0.568(7) | 1.288(29) | −2.723(16) |
| $O_1$ | 2.89 | 0.000 | −2.06 |
| $O_2$ | −0.93 | −2.12 | −3.43 |
| $O_3$ | −0.93 | 2.12 | −3.43 |

[a] The oxygen coordinates were obtained by assuming a linear Fe–C–O geometry and $r(C–O) = 1.149$ Å. The $H_3$ and $H_4$ atoms were fixed in the butadiene plane with $r(H_3–C_2) = r(H_4–C_3) = 1.09$ Å as described earlier. Coordinates without indicated uncertainties were obtained from other work or symmetry considerations. The listed uncertainties are 2σ.

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(16) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra, Techniques of Chemistry*; Wiley: New York, Vol. 18, Chapter 13.

**Table XI.** Proton Chemical Shifts ($\delta$) and Coupling Constants for 5% (Butadiene)iron Tricarbonyl ($BuFe(CO)_3$) in Chloroform-*d* Compared with Values for *trans*-1,3-Butadiene (ref 18)

| parameter | $BuFe(CO)_3$ | *trans*-1,3-butadiene |
|---|---|---|
| $\delta(H_2) = \delta(H_5)$ | 0.27 | 5.04 |
| $\delta(H_1) = \delta(H_6)$ | 1.78 | 5.15 |
| $\delta(H_3) = \delta(H_4)$ | 5.37 | 6.25 |
| $J_{12} = J_{56}$ | 2.50(7) | 1.74 |
| $J_{23} = J_{45}$ | 9.35(6) | 17.05 |
| $J_{13} = J_{46}$ | 6.88(6) | 10.17 |
| $J_{24} = J_{35}$ | −1.15(6) | −0.83 (*AC′*) |
| $J_{14} = J_{36}$ | 1.16(9) | −0.86 (*AB′*) |
| $J_{34}$ | 4.75 | 10.41 (*AA′*) |

[a] The protons are numbered as indicated in Figure 1, with $H_2$ being trans to $H_3$. $H_1$ and $H_2$ are "terminal" protons. $\delta$ values for butadiene were calculated using ref 14 and $\delta$(cyclohexane) = 1.42.

man analysis are in excellent agreement with the structural fit results, and both sets are given in Table IX. The Cartesian coordinates for all atoms are listed in Table X. These coordinates were obtained primarily from the Kraitchman analysis but also using the Fe atom location from the fit results and the fixed values for C–O and $C_2$–$H_3$ bond lengths.

**NMR Measurements.** Proton magnetic resonance spectra of (butadiene)iron tricarbonyl were obtained using a Bruker AM-250 spectrometer. Proton spectra were reported earlier for this complex at lower frequency (and resolution) by Preston and Davis.[17] Spectra were obtained for 5% solutions in chloroform-*d*, benzene-$d_6$, and neat samples. The spectrometer frequency was 250.133 MHz. Resolution enhancement was employed in processing the spectra with parameters GB = 0.2 and LB = −1.5. 32K-point fids were collected with no zero-filling. Best line widths (0.8 Hz) were obtained for the chloroform samples, and the rsults of fitting the spectrum using the LAOCN3 program[19] are shown in Table XI. The digital resolution was 0.15 Hz/pt.

The previous data[17] were helpful in making initial assignments. Final assignments were confirmed by comparisons with spectra of the deuterated butadiene-$d_4$-iron tricarbonyl and by using selective proton-decoupled spectra. The relation between proton chemical shifts and $\pi$-electron densities has been discussed for related compounds,[18] so the measured chemical shifts and coupling constants should provide further information on the structure and bonding in this complex.

We see from the data in Table XI that both chemical shifts and coupling constants are reduced by significant amounts when butadiene is complexed to iron. The proton chemical shifts and coupling constants obtained previously by Hobgood and Goldstein[20] for free *cis*-butadiene are listed for comparison. In most cases, however, the relative order of the values of chemical shifts and coupling constants is retained. The coupling constants listed for $BuFe(CO)_3$ are in very good agreement with earlier results on this complex obtained by Crews.[21] Quantative comparisons of chemical shifts are somewhat difficult due to large solvent effects for $BuFe(CO)_3$. Measured values are $\delta(H_2)$, $\delta(H_1)$, $\delta(H_3)$ = 0.3, 1.8, 5.4 for 5% chloroform solution, −0.2, 1.3, 4.6 for 5% in benzene, and 3.1, 4.6, 8.2 for a neat sample. In spite of these difficulties, we note a substantial reduction of the terminal proton chemical shifts for the complex. They are reduced to values typical of aliphatic (or ethanic) protons. The large change in $\delta$ for the terminal protons is consistent with the changes in structure and bonding indicated by the folding of the $CH_2$ group away from the $C_1$–$C_2$ bond direction (angle $\gamma$) discussed above in the structure results. Both of these effects are consistent with a trend toward $sp^3$ hybridization rather than the $sp^2$ hybridization expected for free *trans*-butadiene. The $H_3$ and $H_4$ chemical shifts, however, are moved only 1 ppm toward more shielded values relative to free butadiene. These observations suggest that [$\pi$, di-$\sigma$] interactions between the diene and the Fe atom make major contributions to the olefin–metal bonding description.

The trans, three-bond coupling constant $J_{23}$ has the largest value for both butadiene and $BuFe(CO)_3$. It is reduced significantly for the complex $BuFe(CO)_3$, but it would be difficult to ascribe this entirely to a change in dihedral angle, due to the $\phi$ rotation, since a nearly proportional reduction occurs for the cis coupling constant $J_{13}$. The dependence of H–H vicinal coupling constants on internal angles was analyzed recently by Barfield and Smith.[22] They derived an expression giving the dependence of $^3J_{HH}$ on the dihedral angle *and* the two interbond angles, $\angle H_2$-$C_1$-$C_2$ and $\angle C_1$-$C_2$-$H_3$. This expression predicts the correct trends in $J_{23}$ and $J_{13}$ with predicted values of 8.0 and 5.6, respectively.[23] These values are in reasonably good agreement with the experimental values, considering that effects of complexation to iron are not included in the theory.

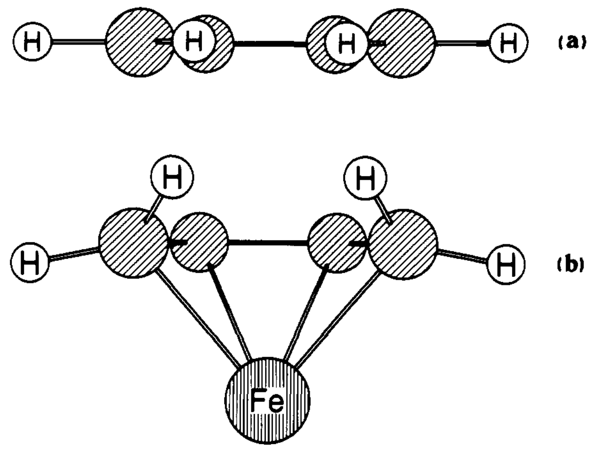

**Figure 3.** Comparison of the free butadiene structure (a) shown in a cis conformation compared with butadiene in the Fe complex (b).

## Discussion of the Structure.

We have obtained 30 rotational constants for 10 isotopomers of (butadiene)iron tricarbonyl using pulsed-beam FT microwave spectroscopy. These data were analyzed using the Kraitchman equations and a fit procedure to obtain a nearly complete set of structure parameters. Only the carbonyl C–O and butadiene $C_2$–$H_3$ and $C_3$–$H_4$ bond lengths were constrained to values determined in other work.[2,15] It appears that significantly better precision and, hopefully, accuracy is obtained from the Kraitchman method for parameters which can be directly compared. For a complete structure description, however, we must use fit results to obtain the Fe coordinates in the principal axis coordinate system. This is not expected to introduce further error into the other coordinates, however. Differences between the optimized least-squares parameters and the corresponding Kraitchman coordinates are believed to be negligible for the heavy atoms which undergo small amplitude zero-point vibrations. Larger discrepancies for some of the hydrogen atom coordinates may be in part due to vibrational averaging effects which contribute differently in the two methods.

The indicated statistical uncertainties in Kraitchman-derived parameters listed in Table IX are approximately a factor of 10 smaller than uncertainties on similar parameters listed in Table VIII, from fit results. Therefore, the coordinates given in Table X are derived primarily from the Kraitchman results, except for cases where a Kraitchman-derived parameter was not obtained. The source of the statistical uncertainties for both the fit results and Kraitchman analysis is primarily due to "model errors" in fitting the experimental results to a rigid, isotopically invariant structure. Propagated errors from the measurements alone would be 1 to 2 orders of magnitude smaller than those listed for Kraitchman results. Estimated uncertainties on the parameters determined in this work are given in Table X.

Perhaps the most interesting features of this structure are the changes in the diene geometry which occur upon complexation with the metal. These are shown in Figure 3. Microwave measurements[15] of free gas-phase *cis*-butadiene indicate that $r(C_1$–$C_2) = 1.337$ and $r(C_2$–$C_3) = 1.467$ Å. The present measurements reveal a reversal in this order upon complex formation: $r(C_1$–$C_2) = 1.42$ and $r(C_2$–$C_3) = 1.41$ Å. These trends were also observed in the solid state by Mills and Robinson,[7] in which $r(C_1$–$C_2) = 1.46$ and $r(C_2$–$C_3) = 1.45$ Å. These observations suggest that [$\pi$, di-$\sigma$] interactions between the diene and the Fe

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(19) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863; Castellano, S; Bothner-By, A. A. *LAOCN3*, QCPE 111.
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(21) Crews, P. *J. Am. Chem. Soc.* **1973**, *95*, 636.
(22) Barfield, M.; Smith, W. B. *J. Am. Chem. Soc.* **1992**, *114*, 1574.
(23) Barfield, M., private communication.

atom make significant contributions to this olefin–metal bonding description. The most dramatic structural changes are in the terminal methylene H coordinates. Ab initio calculations[24] on the free gas-phase structure depict *cis*-butadiene as planar ($\phi$ = 0.0° and $\gamma$ = 0.0°) with bond angles $H_1$–$C_1$–$C_2$ = 121.5° and $H_2$–$C_1$–$C_2$ = 121.6°. In contrast, the structure of the Fe complex of butadiene is characterized by very large changes in these parameters: $\phi$ = 28.1°, $\gamma$ = 26.6°, with bond angles $H_1$–$C_1$–$C_2$ = 112.1° (Kraitchman analysis) or 117.5° (least-squares analysis) and $H_2$–$C_1$–$C_2$ = 118.6° (Kraitchman analysis) or 117.8° (least-squares analysis). These changes in both the carbon skeleton and the terminal hydrogen coordinates are consistent with a trend in which the terminal $sp^2$-hybridized carbon atoms of free butadiene acquire more $sp^3$ character upon complexation with Fe.

The NMR data provide further evidence for these changes in the electronic structure of the olefin. The observed chemical shifts for the terminal methylene protons go from $\delta(H_2)$ = 5.04 and $\delta(H_1)$ = 5.15 ppm in the free butadiene to 0.27 and 1.78 ppm, respectively, in the Fe complex measured in $CDCl_3$. Larger magnitude shifts were observed in benzene solutions, and somewhat smaller shifts were observed in neat solutions. Although the free butadiene values are typical of protons influenced by the diamagnetic deshielding effects of $\pi$-electron densities, the corresponding chemical shifts in the Fe complex are more representative of ordinary aliphatic protons.

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# Chemoselectivity in the Ruthenium-Catalyzed Redox Isomerization of Allyl Alcohols

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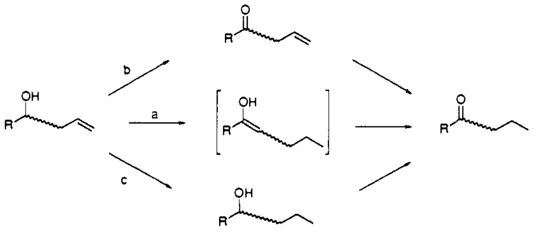
**Abstract:** Adjustment of oxidation level by internal hydrogen reorganization represents a highly efficient synthetic protocol. Cyclopentadienylbis(triphenylphosphine)ruthenium chloride in the presence of triethylammonium hexafluorophosphate catalyzes the redox isomerization of allyl alcohols to their saturated aldehydes or ketones. High chemoselectivity is observed since simple primary and secondary alcohols and isolated double bonds are not affected by this catalyst. The reaction is sensitive to the degree of substitution on the double bond and requires relatively unhindered olefins. Switching to indenylbis(triphenylphosphine)ruthenium chloride in the presence of triethylammonium hexafluorophosphate significantly expands the scope of the reaction to substrates bearing more substituted olefinic linkages and to cyclic substrates of rings containing eight or more members. The mechanism is probed by deuterium labeling, which shows that the metal catalyzes an intramolecular 1,3-hydrogen shift of the carbinol hydrogen to the terminal olefinic position.

Double-bond isomerizations, a process promoted by many transition metals either via a $\pi$-allylmetal intermediate or via a hydrometalation–dehydrometalation, constitute the equivalent of internal reduction–oxidation (redox).[1-10] In those cases where such isomerizations produce olefins possessing hydroxyl groups, irreversible tautomerization can occur to generate ketones to constitute a disproportionation between an alcohol and an olefin (eq 1a). Rearranging the oxidation levels in such a manner represents a more atom economical approach to redox chemistry than processes which involve sequential oxidation and reduction (eq 1b) or vice versa (eq 1c). Surprisingly, this conceptually attractive strategy has found little use synthetically. The lack of chemoselectivity may account for this fact. For example, 9-undecen-1-ol isomerizes to decanal in the presence of an iron carbonyl catalyst.[2] While this example shows the potential of moving a double bond over many carbons before capturing it irreversibly by tautomerization of an enol, it highlights the reactivity of all double bonds under the reaction conditions.



(1)

Such metal-catalyzed redox reactions of unsaturated alcohols need not occur via double-bond isomerizations. An alternative mechanism envisions interaction of the metal with alcohol to form M–H bonds via $\beta$-elimination of a metal alkoxide (or a metal–hydroxyl group complex), which then delivers the hydrogen to the olefin. An analogous process appears to be operating in the isomerization of allylamines to enamines.[10]

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