

## Rotational Spectrum and Internal Rotation of Tricarbonyl(isoprene) Iron

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The microwave spectrum of the  $^{56}\text{Fe}$  and the  $^{54}\text{Fe}$ -isotopomer of tricarbonyl(isoprene) iron was recorded in the range 3–23 GHz using a Fourier transform microwave spectrometer working on a molecular beam. In all, 326 frequencies were measured for the  $^{56}\text{Fe}$ -isotopomer, where some transitions revealed a splitting due to the internal rotation of the methyl group in the diene ligand. Fitting these frequencies to the calculated spectrum yielded rotational constants, centrifugal distortion constants, and a barrier for the internal rotation with high accuracy. For the  $^{54}\text{Fe}$ -isotopomer, 23 transitions could be measured giving another three rotational constants. Here, the centrifugal distortion constants were constrained to the values obtained for the main isotopomer. The six rotational constants can be used to determine the most uncertain structural parameters starting from a geometry based on the structure of the tricarbonyl(butadiene-1,3) iron.

### Introduction

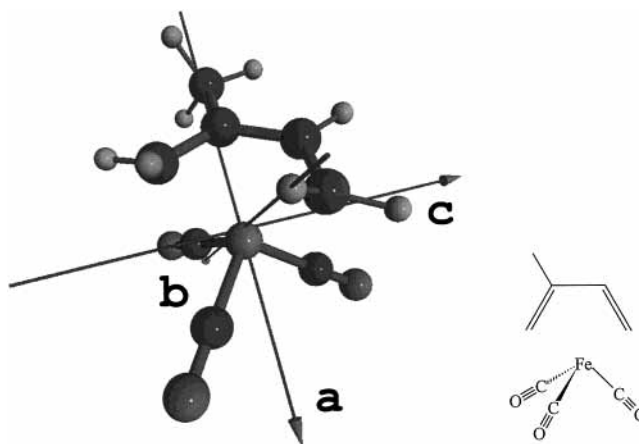
Transition metal carbonyls play a decisive role in many important industrial processes.<sup>1</sup> The Monsanto process for acetic acid production,<sup>2</sup> the homogeneous hydrogenation with the Wilkinson catalyst,<sup>3</sup> the hydroformylation for the functionalization of alkenes into aldehydes,<sup>4,5</sup> the different forms of the Fischer–Tropsch synthesis by which synthetic fuel could be produced, the water conversion with CO yielding molecular hydrogen,<sup>6,7</sup> and the Reppe carbonylation<sup>8</sup> for the polyacryl production are only some of them. In all these reactions the transition metal complexes act as catalysts.

A second interesting point in transition metal chemistry is that their carbonyls have very interesting structures rising from the special bonding situation which is based on coordinative bonds between the central atom and its ligands. These coordinative bonds can be  $\pi$ -bonds to en and diene ligands.

The compound studied in this work, tricarbonyl(isoprene) iron, has an additional remarkable property. It is chiral, i.e., it exists in two enantiomeric forms. Therefore, it can be synthesized in an asymmetric way yielding one enantiomer in excess so that the compound is optically active. This chiral catalyst can now be used for performing other asymmetric synthesis so that two main principles of modern chemistry, catalysis and asymmetric synthesis, are combined giving a mighty tool to the chemist doing preparative chemistry. Grée gave an excellent review article of what can be done with these tools.<sup>9</sup> The synthesis of cycloheptanones from  $\alpha,\alpha'$ -dibromoketones and 1,3-dienes via transition metal complexes is an additional example.<sup>10</sup>

### Experimental Section

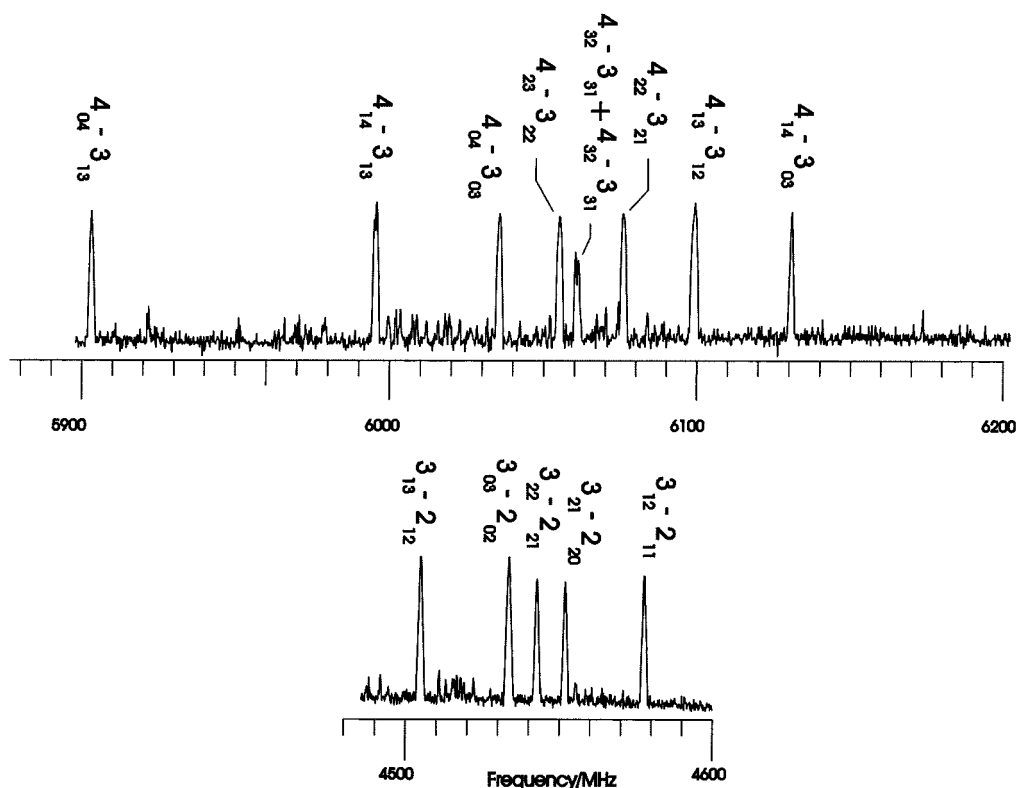
The rotational spectrum of tricarbonyl(isoprene) iron (Figure 1) was recorded in the range from 3 to 23 GHz using a Balle–Flygare-type microwave spectrometer which has been described before.<sup>11</sup> The sample was synthesized from iron nonacarbonyl and isoprene in pentane at a temperature of 50 degrees under dry nitrogen. After 6 h, the solvent was removed and the crude product was purified by chromatography over aluminum oxide. Later measurements revealed that this last purification is not necessary for recording the spectra. Impurities which consist



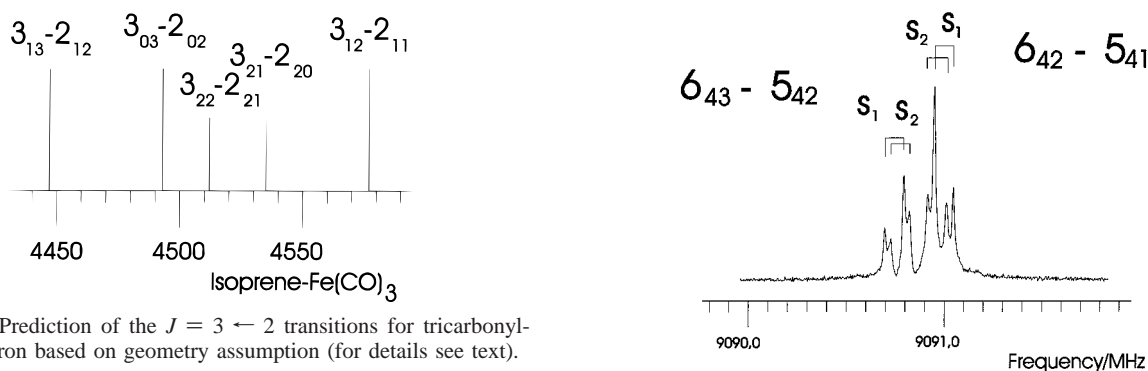
**Figure 1.** Tricarbonyl(isoprene) iron in its principal inertial axes system.

mainly of the green dodecacarbonyl just increase the time after which the sample transitions can be observed. This is probably due to the fact that the dodecacarbonyl is distilled off at the beginning and afterward the pressure of the tricarbonyl(isoprene) iron is sufficient for spectroscopy. This is supported by the change of color of the sample from light green to yellow at the end of the measurements. Heating of the reservoir in front of the nozzle to a temperature of 50–60 °C led to the best results.

The first broad-band scans were done in spectral regions where transitions were predicted by a calculation using an assumed geometry. This geometry was based on the structure which was determined by Kukolich and co-workers for the tricarbonyl(butadiene-1,3) iron.<sup>12,13</sup> It was modified by introducing a methyl group in the 2-position of the butadiene-1,3. The C–C<sub>CH3</sub> bond length was chosen to be 1.501 Å (as in the free isoprene), and the protons of the methyl group were added with a bond length of 1.09 Å and a bond angle of 109.47°. These first scans showed a series of very strong lines (Figure 2). Those for the  $J = 3 \leftarrow 2$  transitions were in good agreement with the predicted ones (Figure 3) so that the assignment of the rotational transitions could be done immediately.



**Figure 2.** Broad-band scans for tricarbonyl(isoprene) iron. The range from 4.48 to 4.60 and from 5.88 to 6.20 GHz is shown with the assigned rotational transitions  $J, K_a', K_c' \leftarrow J, K_a, K_c$ .



**Figure 3.** Prediction of the  $J = 3 \leftarrow 2$  transitions for tricarbonyl(isoprene) iron based on geometry assumption (for details see text).

Some of the rotational transitions had a fine structure which is caused by the internal rotation of the methyl group. This leads to a splitting of the rotational transitions which is largest for those with a high “good”  $K$  quantum number and a high  $J$ . For example  $J, K_a, K_c = 4, 3, 2 \leftarrow 3, 3, 1$  has a good resolved splitting (see also Table 3). Unfortunately for a near symmetric top (asymmetry parameter for tricarbonyl(isoprene) iron  $\kappa = -0.76$ ) there are always two such transitions lying close together (Figure 4), again this closeness rises with high “good”  $K$  quantum number and high  $J$ . This leads to a number of four transitions lying close together, not considering the additional Doppler splitting caused by the experimental technique (Figure 4). Therefore, there are several possibilities to assign the internal rotation splitting. Thus, the transitions had to be measured up to a rather high  $J$  quantum number first in order to determine the centrifugal distortion parameters very accurately. This gave us the exact center frequencies for the hypothetical pure rotational transitions. By this way, it could be identified unambiguously which of the four transition frequencies of such close lying rotational transitions belonged to one internal rotation pattern. The a-type and b-type spectrum was recorded up to a  $J = 15$ , and the c-type spectrum was measured up to  $J = 10$ . This could

**Figure 4.** Internal rotation fine structure for  $J, K_a, K_c = 6, 4, 3 \leftarrow 5, 4, 2$  and  $6, 4, 2 \leftarrow 5, 4, 1$  for tricarbonyl(isoprene) iron (S1 is the A-species, S2 the E-species; the brackets indicate the Doppler splitting, which is caused by experimental technique and is no molecular fine structure).

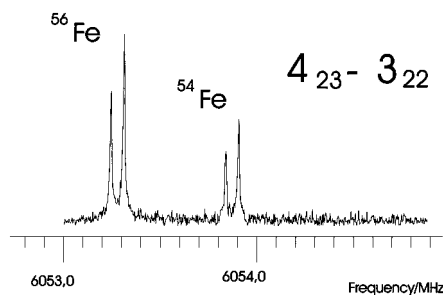
be done without leaving our available spectral range as this molecule is rather heavy. This leads to large moments of inertia and small rotational constants (all smaller than 1 GHz).

So besides the rotational constants and the centrifugal distortion constants the barrier for internal rotation of the methyl group could be gained from the fit of calculated spectra to the measured lines. In this fit, the orientation of the internal rotation axis was fixed to the values derived from the assumed geometry.

After the spectrum of the main isotopomer was understood, some smaller lines which occurred in most cases shifted toward higher frequency compared to the main isotopomer transitions (Figure 5) also could be identified. These are the transitions of the  $^{54}\text{Fe}$ -isotopomer (natural abundance of 5.8%), again in good agreement with the structure assumption.

### Analysis

The fit of the experimental data of the main isotopomer of tricarbonyl(isoprene) iron was performed using an asymmetric



**Figure 5.** High-resolution spectrum for the  $^{54}\text{Fe}$ -isotopomer of tricarbonyl(isoprene) iron. The rotational transition  $4,2,3 \leftarrow 3,2,2$  is shown for the two iron isotopomers.

**TABLE 1: Spectroscopic Parameters for Tricarbonyl(isoprene) Iron**

	$^{56}\text{Fe}$		$^{54}\text{Fe}$	
Rotational Constants				
<i>A</i>	950.897924 (33)	MHz	950.895971 (25)	MHz
<i>B</i>	769.308864 (13)	MHz	769.382604 (11)	MHz
<i>C</i>	744.491151 (14)	MHz	744.565725 (10)	MHz
Centrifugal Distortion Constants (van Eijck)				
<i>D<sub>J</sub></i>	0.05429 (4)	kHz		
<i>D<sub>JK</sub></i>	0.02741 (12)	kHz		
<i>D<sub>K</sub></i>	0.04263 (30)	kHz		
$\delta_J$	-0.00317 (3)	kHz		
<i>R<sub>6</sub></i>	-0.00250 (2)	kHz		
Rotational Barrier <i>V</i> <sub>3</sub>				
	26117	(50)	GHz	
	10.42	(2)	kJ/mol	
	871.2	(1.7)	cm <sup>-1</sup>	
asymmetry parameter $\kappa$	-0.76		-0.76	
representation	<i>I<sup>R</sup></i>		<i>I<sup>R</sup></i>	

top Hamiltonian with centrifugal distortion terms according to van Eijck/Typke<sup>14</sup> and an internal rotation model which has been described before.<sup>15</sup> All rotational constants and centrifugal distortion constants could be fitted together with the barrier for internal rotation of the methyl group and are determined well (Table 1). The fact that the orientation of the internal rotation axis did not have to be changed shows that the structure assumption was pretty good (angle between the internal rotation axis and the a principal axis of the moment of inertia system  $\delta = 144.64^\circ$ , and angle between projection of internal rotation axis on *bc*-plane and the *b*-axis  $\epsilon = 13.44^\circ$ ). For the  $^{54}\text{Fe}$ -isotopomer, which could be measured in natural abundance (Figure 5 and Table 4), the transitions were fitted by only varying the rotational constants *A*, *B*, and *C*. Centrifugal distortion constants and internal rotation parameters were fixed to the values of the main isotopomer. This had to be done because only 23 transitions were available for this isotopomer but is reasonable as the principal inertia axis system is rotated only slightly in the  $^{54}\text{Fe}$ -isotopomer. The smaller errors for the rotational constants of the  $^{54}\text{Fe}$ -isotopomer are due to the smaller amount of experimental material. The standard deviation of the frequencies in the fits are 1.8 kHz for the main isotopomer (326 lines) and 1.0 kHz for the  $^{54}\text{Fe}$ -isotopomer (23 lines).

### Structural Parameters

The geometry assumption based on the structure of tricarbonyl(butadiene-1,3) iron proved to be a good starting point. The excellent agreement of predicted and measured spectral patterns for the  $J = 3 \leftarrow 2$  transitions allowed a fast assignment of the transitions (Figures 2 and 3), the rotational constants varied only slightly when they were fitted to the geometry (Table

**TABLE 2: Structural Fitting for Tricarbonyl(isoprene) Iron<sup>a</sup>**

exptl (MHz)	exptl - calcd (kHz)	parameter
$^{56}\text{Fe}$		
<i>A</i> = 950.898	7	distance: diene-Fe 1.7595 $\rightarrow$ 1.7684 Å
<i>B</i> = 769.309	22	distance: C <sub>CH<sub>3</sub></sub> -C2 1.5010 $\rightarrow$ 1.4673 Å
<i>C</i> = 744.491	22	angle: C3-C2-C <sub>CH<sub>3</sub></sub> 120.0 $\rightarrow$ 135.1°
$^{54}\text{Fe}$		
<i>A</i> = 950.895	-4	
<i>B</i> = 769.383	-16	
<i>C</i> = 744.566	-11	

<sup>a</sup> Exptl gives the experimental rotational constants for the  $^{56}\text{Fe}$ - and  $^{54}\text{Fe}$ -isotopomer. In the second row it is shown how good the fitted geometry reproduces the rotational constants. The parameters which had to be fit to achieve this are given in the last two rows. The numbering of the C atoms follows the tricarbonyl(butadiene-1,3) iron<sup>13</sup>. The starting values are taken from this source, too. The distance diene-Fe is explained in the text.

**TABLE 3: Frequencies for Tricarbonyl(isoprene) Iron (S1, A-Species; S2, E-Species of Internal Rotation Splitting)<sup>a</sup>**

<i>J'</i>	<i>K'<sub>p</sub></i>	<i>K'<sub>o</sub></i>	<i>J</i>	<i>K<sub>p</sub></i>	<i>K<sub>o</sub></i>	symm	calcd GHz	obsd - calcd kHz	obsd GHz
2	1	1	1	1	0	S1	3.0524161	-0.0011	3.0524150
2	1	2	1	1	1	S1	3.0027805	0.0003	3.0027807
2	0	2	1	0	1	S1	3.0252245	-0.0011	3.0252234
3	0	3	2	0	2	S1	4.5320396	0.0001	4.5320397
3	2	1	2	2	0	S1	4.5507482	-0.0015	4.5507467
3	2	2	2	2	1	S1	4.5413939	-0.0007	4.5413932
3	1	2	2	1	1	S1	4.5770595	0.0006	4.5770601
3	1	3	2	1	2	S1	4.5027484	0.0001	4.5027485
4	1	3	3	1	2	S1	6.0996221	-0.0002	6.0996219
4	3	1	3	3	0	S1	6.0603846	0.0038	6.0603884
4	1	4	3	1	3	S1	6.0012007	0.0000	6.0012007
4	3	2	3	3	1	S1	6.0595336	-0.0012	6.0595324
4	3	2	3	3	1	S2	6.0595506	-0.0010	6.0595495
4	0	4	3	0	3	S1	6.0326493	0.0002	6.0326495
4	2	2	3	2	1	S1	6.0758643	-0.0009	6.0758634
4	2	3	3	2	2	S1	6.0533355	0.0009	6.0533364
5	2	3	4	2	2	S1	7.6057237	0.0007	7.6057244
5	2	4	4	2	3	S1	7.5637019	-0.0003	7.5637016
5	1	4	4	1	3	S1	7.6190757	-0.0008	7.6190749
5	3	2	4	3	1	S1	7.5786788	-0.0033	7.5786755
5	1	5	4	1	4	S1	7.4979247	0.0002	7.4979249
5	3	3	4	3	2	S1	7.5757385	0.0004	7.5757388
6	1	5	5	1	4	S1	9.1341535	-0.0004	9.1341531
6	3	3	5	3	2	S1	9.0998437	-0.0001	9.0998437
6	1	6	5	1	5	S1	8.9928998	0.0005	8.9929003
6	3	4	5	3	3	S1	9.0921891	0.0005	9.0921896
6	5	2	5	5	1	S1	9.0887044	0.0012	9.0887056
6	0	6	5	0	5	S1	9.0163231	0.0007	9.0163238
6	2	4	5	2	3	S1	9.1383124	-0.0005	9.1383119
6	4	2	5	4	1	S1	9.0909941	-0.0038	9.0909903
6	4	2	5	4	1	S2	9.0909601	0.0001	9.0909602
6	2	5	5	2	4	S1	9.0721393	0.0003	9.0721396
6	4	3	5	4	2	S1	9.0907410	0.0000	9.0907411
6	4	3	5	4	2	S2	9.0907745	-0.0021	9.0907723
7	0	7	6	0	6	S1	10.5033048	0.0001	10.5033049
7	2	5	6	2	4	S1	10.6707289	-0.0004	10.6707285
7	4	3	6	4	2	S1	10.6088577	-0.0006	10.6088570
7	6	1	6	6	0	S1	10.6031877	0.0040	10.6031917
7	2	6	6	2	5	S1	10.5783485	-0.0001	10.5783484
7	4	4	6	4	3	S1	10.6080238	0.0002	10.6080240
7	1	6	6	1	5	S1	10.6434600	-0.0004	10.6434596

<sup>a</sup> The full list is available as Supporting Information.

2) and even the orientation of the internal rotation axis did not have to be varied during the fit so that it could be fixed to the values according to the structure assumption.

The geometry of tricarbonyl(butadiene-1,3) iron which was determined by Kukulich et al.<sup>13</sup> was based on the information on 10 different isotopomers, among them all <sup>13</sup>C-isotopomers

**TABLE 4: Frequencies for  $^{54}\text{Fe}$ -Isotopomer of Tricarbonyl(isoprene) Iron (S1, A-Species; S2, E-Species of Internal Rotation Splitting)**

$J'$	$K_p'$	$K_o'$	$J$	$K_p$	$K_o$	symm.	calcd GHz	obsd - calcd kHz	obsd GHz
3	0	3	2	0	2	S1	4.5324816	0.0003	4.5324818
3	2	1	2	2	0	S1	4.5511961	0.0007	4.5511967
3	2	2	2	2	1	S1	4.5418389	0.0024	4.5418413
3	1	2	2	1	1	S1	4.5775026	0.0001	4.5775027
3	1	3	2	1	2	S1	4.5031942	-0.0005	4.5031937
4	1	3	3	1	2	S1	6.1002118	0.0000	6.1002117
4	1	4	3	1	3	S1	6.0017944	0.0004	6.0017948
4	0	4	3	0	3	S1	6.0332360	0.0008	6.0332368
4	2	2	3	2	1	S1	6.0764634	0.0001	6.0764635
4	2	3	3	2	2	S1	6.0539282	0.0013	6.0539295
5	2	3	4	2	2	S1	7.6064739	-0.0011	7.6064728
5	2	4	4	2	3	S1	7.5644418	-0.0009	7.5644409
5	1	4	4	1	3	S1	7.6198106	0.0004	7.6198111
5	3	2	4	3	1	S1	7.5794241	-0.0016	7.5794225
5	1	5	4	1	4	S1	7.4986661	0.0002	7.4986663
5	3	3	4	3	2	S1	7.5764818	0.0009	7.5764827
6	0	6	5	0	5	S1	9.0172001	0.0000	9.0172001
7	4	4	6	4	3	S1	10.6090656	0.0008	10.6090664
11	3	9	10	3	8	S1	16.6619667	-0.0016	16.6619652
4	0	4	3	1	3	S1	5.9034533	0.0009	5.9034542
4	1	4	3	0	3	S1	6.1315772	-0.0003	6.1315769
4	3	2	3	2	1	S1	7.0194138	-0.0013	7.0194126
4	3	1	3	2	2	S1	7.0321399	0.0015	7.0321413

and several deuterated isotopomers, so that one of the best gas-phase structures that ever has been determined for such a large molecule could be derived.

The obtained rotational constants of the  $^{56}\text{Fe}$ - and the  $^{54}\text{Fe}$ -isotopomer were then used to improve the structure of the tricarbonyl(isoprene) iron. The internal coordinates which were fitted to reproduce the experimental rotational constants were the distance from the central iron atom to the butadiene plane (exactly the center of the trapezoid formed by the four carbon atoms of the diene), the C-CH<sub>3</sub> bond length and the C-C-CH<sub>3</sub> bond angle. All available six rotational constants of the two isotopomers were fitted by varying these coordinates. The results are given in Table 2, where the starting values for the fitted internal coordinates are listed too. These were chosen according to the geometry of the tricarbonyl(butadiene-1,3) iron.<sup>13</sup> It can be seen that the distance from the diene ligand to the central iron atom seems to get larger when butadiene-1,3 is replaced by isoprene. This is reasonable as the larger isoprene ligand takes up more space. The distance of the methyl group to the carbon backbone is smaller than in the free isoprene. This distortion of the diene ligand on complexation to the iron atom is in agreement with the results found for the tricarbonyl(butadiene-1,3) iron. Three remarkable structural properties had been found for this molecule. First, there is no local C<sub>3</sub> symmetry of the tricarbonyl part. This can be imagined by a distortion of this tricarbonyl group so that only a mirror plane results. A better and more visual description of this complex is that of a tetragonal pyramid where the top of the pyramid is taken by one CO and the other two CO ligands and the former double bonds of the diene via  $\pi$ -bonds take the four positions of the base of this pyramid. The second point is that the diene ligand is not planar in this complex. The hydrogens at the end of the carbon chain are twisted out of the plane. This is assured clearly by the very good structure determination in ref 13. This nonplanarity together with the third point, the change of C-C-bond lengths, is a clear hint to the changes in the ligand on complexation. The carbon-carbon bond lengths change in the way that the former single bonds are shortened to 1.409 Å (1.467 Å in the free isoprene) and the former double bonds are lengthened to 1.385 Å (1.337 Å in the free isoprene). These

structural changes go together with a change of electronic density and a change of electronic energy levels so that the catalytic activity and the different reactivity of the dienes in such ligands can be explained very nicely.

The value obtained for the C-C-C<sub>CH<sub>3</sub></sub> bond angle probably is too large, though the value for the free isoprene of 120.0° is assumed and not fitted.

## Discussion

In this work, the first example of a chiral diene iron tricarbonyl has been studied by microwave spectroscopy after Kukolich and co-workers had given a structure for the nonchiral tricarbonyl(butadiene-1,3) iron. Of course, the derived structural parameters cannot be taken as absolute values as there were only six rotational constants and the molecule has  $3N - 6$  internal coordinates ( $N = 20$ ). So the fitted coordinates can just be used for comparisons with other molecules in this series of diene iron tricarbonyls. Some of them will be published soon. Work that has to be done in the future in order to improve this structure includes measuring the spectra of more isotopomers and the performance of ab initio calculations to avoid weaknesses of microwave structures such as lack of experimental information in comparison with the number of internal parameters and the correlation of internal parameters during structure fitting.

The obtained barrier of internal rotation of  $V_3 = 26117$  GHz (10.42 kJ/mol) also has to be seen in comparison with other molecules. It is much larger than the barrier in tricarbonyl(methylcyclopentadienyl) manganese ( $V_3 = 17000$  GHz). A possible explanation is the smaller distance of the ligand toward the central atom and thus more effective steric hindering of the internal motion. Another interesting reason could be a partial double bond character of the C-C<sub>CH<sub>3</sub></sub> bond which results from mesomerism.

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**Supporting Information Available:** The full frequency list for the main isotopomer of tricarbonyl(isoprene) iron. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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