Measurements of structural and quadrupole coupling parameters for bromoferrocene using microwave spectroscopy

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Rotational spectra for two isotopomers of bromoferrocene were measured using pulsed-beam Fourier transform microwave spectroscopy. Transitions were observed for the ^{79}Br and ^{81}Br isotopomers in the 5–9 GHz range. Rotational constants and the quadrupole coupling tensors were obtained from the data. The rotational constants and quadrupole coupling parameters for ^{79}Br are $A=1272.110(1)$, $B=516.1125(2)$, $C=441.3775(2)$, $eQq_{aa}=267.16(3)$, $eQq_{ab}=-409.81(4)$, and $eQq_{bb}=21.49(4)$, and those for ^{81}Br are $A=1271.045(4)$, $B=510.0079(2)$, $C=436.7687(2)$, $eQq_{aa}=225.40(6)$, $eQq_{ab}=-341.62(4)$, and $eQq_{bb}=15.65(4)$. The measured rotational constants were used to determine the following structural parameters of bromoferrocene: $r(\text{Fe}-(\text{C}_5\text{H}_5))=1.63(2)$, $r(\text{Fe}-(\text{C}_5\text{H}_4\text{Br}))=1.67(3)$, $r(\text{C}-\text{Br})=1.875(11)$, and $r(\text{C}-\text{C})=1.433(1)$ Å. The values of the quadrupole coupling parameters in the principal quadrupole axis systems and the C–Br bond axis systems are compared with similarly derived parameters for chloroferrocene, chlorobenzene, and bromobenzene. Previous data for chloroferrocene has been reanalyzed to obtain refined quadrupole parameters. © *1997 American Institute of Physics.* [S0021-9606(97)03241-8]

INTRODUCTION

The characterization of the structure and bonding of ferrocene by Wilkinson[1] was an important step in the development of organometallic chemistry. The unusual and unexpected π bonding of the cyclopentadienyl radical (Cp) to metals resulted in surprisingly stable complexes, of which an enormous number of examples have been studied since the initial work in the early 1950's. Ferrocene and ferrocene derivatives have been of considerable interest and widely studied in order to characterize this type of bonding. It has been shown from electron diffraction measurements[2] that the gas-phase ferrocene structure is very similar to the well known solid state ''sandwich'' structure from x-ray work. This same basic structure was obtained in a previous gas-phase microwave study of chloroferrocene.[3] No previous gas-phase structure determinations had been done on substituted ferrocenes prior to the study of chloroferrocene. The only previous spectroscopic studies of bromoferrocene were done with Mössbauer spectroscopy[4] in the solid phase. Bonding in the ferrocene complexes is also of interest because the η^5-type π bonding is observed for a wide range of complexes where a Cp group is bound to a metal atom. Both chlorine and bromine contain quadrupolar nuclei. Coupling of these nuclear quadrupole moments with the electric field gradients is observed as line splitting in the microwave spectrum and can be used to investigate and characterize the bonding in these complexes. In this report, the data for bromoferrocene have been used to determine effects of bonding interactions between the Br atom and the Cp ring. Previous data on chloroferrocene have been reanalyzed with the aid of new data obtained on chlorobenzene. New measurements were made for chlorobenzene so that better quadrupole parameters would be available for comparison with chlorofer-

rocene. The quadrupole coupling in these compounds will be discussed, as it reveals information on the bonding interactions in the compounds.

EXPERIMENT

Preparation of chloroferrocene was reported previously.[3] The chlorobenzene sample was purchased from Aldrich and used without further purification. The preparation of bromoferrocene was performed in two phases. The first phase was the preparation of chloromercuriferrocene, which was then reacted with N-bromosuccinimide in the second phase to produce bromoferrocene. The method chosen was adapted from the method described by Fish and Rosenblum.[5]

Synthesis

Chloromercuriferrocene

A solution of 46.5 g of ferrocene in 250 mL of benzene was reacted with a solution of 40 g of mercuric acetate in 375 mL of methanol for 10 h under inert atmosphere. Subsequently, a solution of 11 g of lithium chloride in 100 mL of a 50% ethanol-water mixture was added dropwise to the reaction vessel, resulting in a bright orange precipitate. This mixture was then stirred for 2 h, followed by 1 h of reflux. The crude chloromercuriferrocene was extracted with methylene chloride in a soxhlet extractor and any remaining ferrocene was removed by sublimation. The resulting product was in the form of golden yellow plates.

Bromoferrocene

A solution of 1.2 g of N-bromosuccinimide in 100 mL of dimethylformamide was reacted with a solution of 2 g of chloromercuriferrocene in 50 mL of dimethylformamide at 0 °C with stirring. This solution was allowed to react under inert atmosphere for 3 h. Then, 200 mL of 10% aqueous

TABLE I. Measured and calculated frequencies (MHz) for the ^{79}Br isotopomer of bromoferrocene. Listed errors in the frequencies are 1σ. ''Int.'' is the approximate relative intensity in millivolts of signal.

Measured	Calculated	Difference	Int.	$J'_{Kp'Ko'}$	$2F'$	J_{KpKo}	$2F$
5579.8359(07)	5579.831 82	0.004 08	25	6_{06}	15	5_{05}	13
5581.2359(18)	5581.234 56	0.001 34	15	6_{06}	9	5_{05}	7
5586.3579(16)	5586.355 64	0.002 26	18	6_{06}	13	5_{05}	11
5588.8763(12)	5588.874 44	0.001 86	05	6_{06}	11	5_{05}	9
5724.5360(07)	5724.530 97	0.005 03	18	6_{25}	13	5_{24}	11
5763.2472(25)	5763.246 64	0.000 56	10	6_{34}	15	5_{33}	13
5775.4140(16)	5775.414 86	−0.000 86	05	6_{33}	15	5_{32}	13
5777.7230(26)	5777.719 63	0.003 37	05	6_{34}	11	5_{33}	9
5788.3117(39)	5788.318 52	−0.006 82	10	6_{33}	11	5_{32}	9
5790.7777(22)	5790.778 03	−0.000 33	05	6_{34}	13	5_{33}	11
5801.8840(08)	5801.881 66	0.002 34	07	6_{33}	13	5_{32}	11
6186.6206(42)	6186.620 13	0.000 47	20	7_{07}	15	6_{16}	13
6191.1825(24)	6191.183 87	−0.001 37	15	7_{07}	13	6_{16}	11
6191.9795(27)	6191.979 59	−0.000 09	18	7_{07}	17	6_{16}	15
6382.5410(10)	6382.543 45	−0.002 45	20	7_{17}	17	6_{16}	15
6384.5897(15)	6384.594 93	−0.005 23	08	7_{17}	11	6_{16}	9
6385.2881(09)	6385.290 95	−0.002 85	12	7_{17}	15	6_{16}	13
6388.2064(21)	6388.210 40	−0.004 00	20	7_{17}	13	6_{16}	11
6463.2950(14)	6463.293 95	0.001 05	25	7_{07}	17	6_{06}	15
6464.3443(10)	6464.344 93	−0.000 63	17	7_{07}	11	6_{06}	9
6469.2470(13)	6469.247 14	−0.000 14	14	7_{07}	15	6_{06}	13
6471.2665(15)	6471.268 21	−0.001 71	18	7_{07}	13	6_{06}	11
6658.7944(28)	6658.745 61	0.004 29	17	7_{26}	17	6_{25}	15
7279.1109(21)	7279.110 06	0.000 84	25	8_{18}	19	7_{17}	17
7280.7266(07)	7280.729 31	−0.002 71	18	8_{18}	13	7_{17}	11
7281.4467(14)	7281.447 31	−0.000 61	20	8_{18}	17	7_{17}	15
7283.8409(20)	7283.842 40	−0.001 50	16	8_{18}	15	7_{17}	13
7340.7205(09)	7240.718 87	0.001 63	23	8_{08}	19	7_{07}	17
7341.4596(28)	7341.459 61	−0.000 01	10	8_{08}	13	7_{07}	11
7345.5250(21)	7345.523 86	0.001 14	25	8_{08}	17	7_{07}	15
7347.4796(26)	7347.482 71	−0.003 11	25	8_{08}	15	7_{07}	13
8214.7271(41)	8214.721 46	0.005 64	20	9_{09}	15	8_{08}	13
8220.0277(59)	8220.029 95	−0.002 25	20	9_{09}	17	8_{08}	15
8309.5416(56)	8309.538 62	0.002 98	04	9_{19}	17	8_{08}	15
8309.7251(84)	8309.726 73	−0.001 63	03	9_{19}	19	8_{08}	17

TABLE II. Measured and calculated frequencies (MHz) for the ^{81}Br isotopomer of bromoferrocene. Listed errors in the frequencies are 1σ. ''Int.'' is the approximate relative intensity in millivolts of signal.

Measured	Calculated	Difference	Int.	$J'_{Kp'Ko'}$	$2F'$	J_{KpKo}	$2F$
5522.5065(08)	5522.509 94	−0.003 44	12	6_{06}	15	5_{05}	13
5523.8310(18)	5523.834 10	−0.003 10	08	6_{06}	9	5_{05}	7
5527.9221(11)	5527.924 29	−0.002 19	20	6_{06}	13	5_{05}	11
5530.0259(14)	5530.029 49	−0.003 59	15	6_{06}	11	5_{05}	9
5708.6738(59)	5708.676 42	−0.002 62	03	6_{34}	11	5_{33}	9
5724.7104(57)	5724.709 11	0.001 29	15	6_{34}	13	5_{33}	11
5734.8851(39)	5734.886 13	−0.001 03	03	6_{33}	13	5_{32}	11
5802.9831(44)	5802.981 11	0.001 99	05	6_{16}	9	5_{05}	7
5803.5785(39)	5803.579 12	−0.000 62	05	6_{16}	15	5_{05}	13
5810.2339(12)	5810.235 85	−0.001 95	12	6_{24}	9	5_{23}	7
5811.8383(03)	5811.838 56	−0.000 26	18	6_{24}	15	5_{23}	13
5812.5495(10)	5812.546 40	0.003 10	40	6_{24}	13	5_{23}	11
5813.8619(22)	5813.859 66	0.002 24	25	6_{24}	11	5_{23}	9
5818.5220(44)	5818.523 45	−0.001 45	05	6_{16}	11	5_{05}	9
5818.6040(25)	5818.602 34	0.001 66	10	6_{16}	13	5_{05}	11
6111.7006(22)	6111.702 05	−0.001 45	04	7_{07}	15	6_{16}	13
6315.3892(06)	6315.384 54	0.004 66	10	7_{17}	17	6_{16}	15
6317.2100(17)	6317.208 37	0.001 63	08	7_{17}	11	6_{16}	9
6317.7099(11)	6317.705 19	0.004 71	10	7_{17}	15	6_{16}	13
6320.1440(17)	6320.141 78	0.002 22	07	7_{17}	13	6_{16}	11
6397.3944(20)	6397.392 39	0.002 01	12	7_{07}	17	6_{06}	15
6398.3881(11)	6398.388 17	−0.000 07	10	7_{07}	11	6_{06}	9
6402.3808(15)	6402.380 10	0.000 70	15	7_{07}	15	6_{06}	13
6404.0415(06)	6404.040 01	0.001 49	10	7_{07}	13	6_{06}	11
7265.9874(20)	7265.988 97	−0.001 57	20	8_{08}	19	7_{07}	17
7266.7497(12)	7266.753 08	−0.003 38	11	8_{08}	13	7_{07}	11
7270.1298(20)	7270.130 52	−0.000 72	13	8_{08}	17	7_{07}	15
7271.6504(09)	7271.651 19	−0.000 79	15	8_{08}	15	7_{07}	13

sodium thiosulfate solution were added to the reaction vessel, resulting in a dark brown solution, and this was poured over 2 L of ice. The crude product was extracted with four 100 mL portions of petroleum ether and dried overnight on magnesium sulfate. The product was recrystallized from methylene chloride and sublimed, leaving golden yellow plates melting at 31–32 °C (lit. mp 30–31 °C).[5] Characterization of this compound was performed on a Nicolet FTIR instrument in a gas cell; infrared transitions typical of a singly substituted ferrocene were observed at 3092.6 (s), 1407.1 (m), 1379.0 (w), 1357.7 (w), 1340.6 (m), 1178.1 (w), 1150.0 (m), 1105.2 (s), 1053.9 (vw), 1018.7 (m), 1008.9 (w), 998.9 (m), 870.4 (m), 815.8 (w), and 806.3 (m). These observed infrared (IR) transitions have not been previously reported but agree well with the analogous IR transitions of chloroferrocene.[3]

Microwave measurements

The microwave spectrum was scanned in the 5–9 GHz range using a Flygare-Balle type spectrometer system.[6] The sample and pulse valve (General Valve 9-181) were maintained at 45–60 °C to produce sufficient vapor pressure of bromoferrocene. The vapor was mixed with neon at 0.6–1.0 atm and pulsed into a Fabry-Perot microwave cavity for observation of the spectra. The microwave pulse length was typically 0.1 μs, and the observed linewidths [full width at half maximum] (FWHM) were about 20 kHz, with the neon carrier gas. The statistical uncertainty in line center measurements ranges from 0.3 to 8.4 kHz, depending on line strength and residual broadening due to unresolved components. This statistical uncertainty (1σ) is given in parentheses for each transition in Tables I–V. Systematic errors are much smaller than this uncertainty, since frequency calibrations were made with respect to WWVH (NIST, VLF Radio Station, Boulder, CO). Transitions of moderate intensity were observed for bromoferrocene, with typical quadrupole splitting patterns of an asymmetric top for $J' \leftarrow J = 6 \leftarrow 5$ through $9 \leftarrow 8$. The measured transitions are listed in Tables I and II. Approximate relative intensities are listed in the ''Int.'' column. The sample of chloroferrocene was rescanned in the $J = 5 \leftarrow 4$ region for better determination of high K quadrupole splitting patterns in the ^{37}Cl isotopomer. Nineteen new transitions were measured, and listed (transitions with *) in Tables III and IV, along with previous data.[3] The previous data[7,8] for chlorobenzene were rather limited, so new measurements were made on chlorobenzene to allow comparison with the results of new analyses of chloroferrocene data. More than 50 new strong transitions for chlorobenzene were measured

TABLE III. Measured and calculated frequencies (MHz) for ^{35}Cl chlorof-errocene. Frequencies marked with an asterisk were not reported in the previous publication (Ref. 3).

Measured	Calculated	Difference	$J'_{Kp'Ko'}$	$2F'$	J_{KpKo}	$2F$
*4129.9856(16)	4129.984 36	0.001 24	3_{03}	7	2_{02}	5
4132.1238(13)	4132.121 06	0.002 74	3_{03}	9	2_{02}	7
5309.5827(20)	5309.581 8	0.000 85	4_{14}	9	3_{13}	7
5310.4115(20)	5310.410 39	0.001 11	4_{14}	11	3_{13}	9
5433.4624(24)	5433.461 18	0.001 22	4_{04}	9	3_{03}	7
5433.5701(53)	5433.565 58	0.004 52	4_{04}	7	3_{03}	5
5435.7688(15)	5435.769 53	−0.000 73	4_{04}	11	3_{03}	9
5435.8720(41)	5435.873 01	−0.001 01	4_{04}	5	3_{03}	3
6474.6984(10)	6474.696 79	0.001 61	5_{05}	7	4_{14}	5
6475.5849(26)	6475.585 53	−0.000 63	5_{05}	9	4_{14}	7
6475.7142(08)	6475.712 13	0.002 07	5_{05}	13	4_{14}	11
6476.6231(05)	6476.621 43	0.001 67	5_{05}	11	4_{14}	9
6610.4943(12)	6610.493 75	0.000 55	5_{15}	9	4_{14}	7
6611.0573(25)	6611.056 95	0.000 35	5_{15}	11	4_{14}	9
6611.2609(15)	6611.260 84	0.000 06	5_{15}	7	4_{14}	5
6611.8120(09)	6611.810 56	0.001 44	5_{15}	13	4_{14}	11
6704.8996(10)	6704.906 16	−0.006 56	5_{05}	9	4_{04}	7
*6704.9292(17)	6704.923 92	0.005 28	5_{05}	11	4_{04}	9
6706.9102(09)	6706.911 04	−0.000 84	5_{05}	13	4_{04}	11
6839.3580(17)	6839.359 44	−0.001 44	5_{15}	11	4_{04}	9
6843.0071(13)	6843.009 47	−0.002 37	5_{15}	13	4_{04}	11
6967.1904(23)	6967.192 93	−0.002 53	5_{24}	11	4_{23}	9
6967.3935(21)	6967.395 55	−0.002 05	5_{24}	9	4_{23}	7
7053.5992(14)	7053.598 13	0.001 07	5_{42}	11	4_{41}	9
7054.8317(68)	7054.833 98	−0.002 28	5_{42}	13	4_{41}	11
*7055.4027(43)	7055.399 19	0.003 51	5_{42}	7	4_{41}	5
7055.9270(35)	7055.929 63	−0.002 63	5_{41}	13	4_{40}	11
7060.8752(13)	7060.876 31	−0.001 11	5_{33}	11	4_{32}	9
7061.1861(22)	7061.186 43	−0.000 33	5_{33}	9	4_{32}	7
7061.5362(43)	7061.536 43	−0.000 23	5_{33}	13	4_{32}	11
7061.8570(41)	7061.854 86	0.002 14	5_{33}	7	4_{32}	5
7097.8129(14)	7097.812 61	0.000 29	5_{32}	13	4_{31}	11
*7097.8515(30)	7097.848 19	0.003 31	5_{32}	11	4_{31}	9
7097.9533(51)	7097.954 99	−0.001 69	5_{32}	7	4_{31}	5
7236.0066(15)	7236.007 47	−0.000 87	5_{14}	11	4_{13}	9
*7485.6887(21)	7485.690 57	−0.001 87	6_{15}	15	5_{24}	13
7827.7669(46)	7827.764 76	0.002 14	6_{06}	9	5_{15}	7
7827.9380(10)	7827.932 65	0.005 35	6_{06}	11	5_{15}	9
7828.3577(79)	7828.360 75	−0.003 05	6_{06}	15	5_{15}	13
7828.5230(15)	7828.516 02	0.006 98	6_{06}	13	5_{15}	11
7901.7355(27)	7901.735 00	0.000 50	6_{16}	11	5_{15}	9
7902.1140(28)	7902.113 85	0.000 15	6_{16}	13	5_{15}	11
7902.4262(14)	7902.424 23	0.001 97	6_{16}	9	5_{15}	7
7902.8149(61)	7902.817 84	−0.002 94	6_{16}	15	5_{15}	13
7962.8366(38)	7962.840 34	−0.003 74	6_{06}	11	5_{05}	9
*7962.9424(40)	7962.950 79	−0.008 39	6_{06}	13	5_{05}	11
9147.0809(47)	9147.077 09	0.003 81	7_{07}	17	6_{16}	15
9184.8262(35)	9184.827 02	−0.000 82	7_{17}	13	6_{16}	11
9185.1118(30)	9185.113 13	−0.001 33	7_{17}	15	6_{16}	13
9185.4451(23)	9185.445 93	−0.000 83	7_{17}	11	6_{16}	9
9185.7383(72)	9185.740 09	−0.001 79	7_{17}	17	6_{16}	15
9220.2996(59)	9220.296 28	0.003 32	7_{07}	13	6_{06}	11
9220.4647(84)	9220.463 49	0.001 21	7_{07}	15	6_{06}	13
*9221.3508(51)	9221.357 70	−0.006 90	7_{07}	11	6_{06}	9
9221.5343(43)	9221.533 51	0.000 79	7_{07}	17	6_{06}	15
*9258.6292(41)	9258.629 90	−0.000 70	7_{17}	13	6_{06}	11
9260.1046(59)	9260.105 40	−0.000 80	7_{17}	11	6_{06}	9
9260.2007(53)	9260.197 17	0.003 53	7_{17}	17	6_{06}	15
10 481.4361(69)	10 481.436 42	−0.000 32	8_{08}	15	7_{07}	13
10 481.6166(23)	10 481.615 48	0.001 12	8_{08}	17	7_{07}	15
10 482.1985(47)	10 482.198 13	0.000 37	8_{08}	13	7_{07}	11
10 482.3892(52)	10 482.383 40	0.005 80	8_{08}	19	7_{07}	17

TABLE IV. Measured and calculated frequencies (MHz) for ^{37}Cl chlorof-errocene. Frequencies marked with an asterisk were not reported in the previous publication (Ref. 3).

Measured	Calculated	Difference	$J'_{Kp'Ko'}$	$2F'$	J_{KpKo}	$2F$
[a]4051.0559(21)	4051.054 46	0.001 44	3_{03}	9	2_{02}	7
*5329.2993(17)	5329.299 91	−0.000 61	4_{04}	9	3_{03}	7
[a]5329.3348(32)	5329.327 95	0.006 85	4_{04}	7	3_{03}	5
*5331.0304(15)	5331.030 04	0.000 36	4_{04}	11	3_{03}	9
[a]5331.0628(33)	5331.056 76	0.006 04	4_{04}	5	3_{03}	3
6480.6339(12)	6480.634 68	−0.000 78	5_{15}	9	4_{14}	7
6481.0839(21)	6481.085 81	−0.001 91	5_{15}	11	4_{14}	9
6481.2293(49)	6481.230 87	−0.001 57	5_{15}	7	4_{14}	5
6481.6716(07)	6481.672 84	−0.001 24	5_{15}	13	4_{14}	11
6577.2304(12)	6577.234 46	−0.004 06	5_{05}	9	4_{04}	7
6577.2746(18)	6577.273 00	0.001 60	5_{05}	11	4_{04}	9
6578.7589(12)	6578.768 14	−0.009 24	5_{05}	7	4_{04}	5
6578.7860(07)	6578.784 71	0.001 29	5_{05}	13	4_{04}	11
6720.6478(11)	6720.647 75	0.000 05	5_{15}	11	4_{04}	9
6720.9874(28)	6720.987 73	−0.000 33	5_{15}	9	4_{04}	7
6723.4833(24)	6723.485 23	−0.001 93	5_{15}	13	4_{04}	11
6723.8351(15)	6723.834 38	0.000 72	5_{15}	7	4_{04}	5
*6826.9742(25)	6826.973 46	0.000 74	5_{24}	11	4_{23}	11
*6828.0860(25)	6828.086 57	−0.000 57	5_{24}	11	4_{23}	9
*6828.2440(75)	6828.250 64	−0.006 64	5_{24}	9	4_{23}	7
*6828.9422(28)	6828.944 27	−0.002 07	5_{24}	13	4_{23}	11
*6829.1042(46)	6829.100 97	0.003 23	5_{24}	7	4_{23}	5
*6830.2752(15)	6830.274 87	0.000 33	5_{24}	7	4_{23}	7
*6917.4946(19)	6917.492 87	0.001 73	5_{33}	13	4_{32}	11
*6917.8036(33)	6917.803 69	−0.000 09	5_{33}	7	4_{32}	5
*6918.3299(17)	6918.329 44	0.000 46	5_{33}	11	4_{32}	11
7094.6459(16)	7094.646 15	−0.000 25	5_{14}	7	4_{13}	5
7666.9366(81)	7666.939 45	−0.002 85	6_{06}	9	5_{15}	7
7667.1074(73)	7667.104 32	0.003 08	6_{06}	11	5_{15}	9
7667.4170(90)	7667.420 21	−0.003 21	6_{06}	15	5_{15}	13
7667.5746(61)	7667.574 96	−0.000 36	6_{06}	13	5_{15}	11
7747.0832(24)	7747.082 86	0.000 34	6_{16}	11	5_{15}	9
7747.3928(48)	7747.387 49	0.005 31	6_{16}	13	5_{15}	11
7747.6143(38)	7747.613 91	0.000 39	6_{16}	9	5_{15}	7
7747.9326(78)	7747.930 49	0.002 11	6_{16}	15	5_{15}	13
7810.8589(16)	7810.857 59	0.001 31	6_{06}	11	5_{05}	9
7810.9474(45)	7810.949 72	−0.002 32	6_{06}	13	5_{05}	11
7812.0094(60)	7812.005 69	0.003 71	6_{06}	9	5_{05}	7
7812.1208(19)	7812.120 73	0.000 07	6_{06}	15	5_{05}	13
9005.4939(33)	9005.491 28	0.002 62	7_{17}	13	6_{16}	11
9006.2051(10)	9006.203 85	0.001 25	7_{17}	17	6_{16}	15
9043.2312(47)	9043.229 91	0.001 29	7_{07}	13	6_{06}	11
9043.3635(36)	9043.364 87	−0.001 37	7_{07}	15	6_{06}	13
9044.0590(63)	9044.059 69	−0.000 69	7_{07}	11	6_{06}	9
9044.1989(63)	9044.200 62	−0.001 72	7_{07}	17	6_{06}	15

[a]These lines were previously reported with different F values. These misas-signments are likely to be the major contribution to the uncertainty in eQq_{aa} reported previously.

in the 4.8 to 6 GHz range. The new data include $J=2\leftarrow1$, R branch and $J=5$, Q branch transitions, and are listed in Table V.

RESULTS AND DATA ANALYSIS

Bromoferrocene

The observed transitions were fit using eight adjustable parameters in the Hamiltonian for each isotopomer. The adjustable parameters were the rotational and distortion constants A, B, C, D_J, and D_{JK} and the quadrupole coupling

TABLE V. Measured transition frequencies for ^{35}Cl- and ^{37}Cl-benzene. ''Meas.–Calc.'' columns list the differences between measured, and the ''best fit'' calculated frequencies. Frequencies are listed in MHz.

^{35}Cl frequency	Meas.–Calc.	^{37}Cl frequency	Meas.–Calc.	$J'_{Kp'Ko'}$	$2F'$	J_{KpKo}	$2F$
5124.1502(36)	0.001 19	4874.1925(16)	0.003 08	5_{14}	11	5_{15}	11
5124.5010(06)	−0.001 91	4874.4669(18)	−0.002 90	5_{14}	9	5_{15}	9
5125.4152(24)	0.000 24	4875.1925(32)	0.002 00	5_{14}	13	5_{15}	13
5125.7672(52)	−0.000 76	4875.4669(18)	−0.003 42	5_{14}	7	5_{15}	7
5264.3192(08)	−0.000 77	5141.8706(08)	−0.001 62	2_{12}	5	1_{11}	3
5270.2307(06)	−0.001 14	5146.5272(19)	−0.002 18	2_{12}	3	1_{11}	3
5273.8702(03)	−0.001 47	5149.4001(06)	−0.000 63	2_{12}	5	1_{11}	5
5278.5059(16)	−0.002 12	5153.0465(21)	−0.002 77	2_{12}	1	1_{11}	3
5279.7813(20)	−0.002 24	5154.0561(23)	−0.001 79	2_{12}	3	1_{11}	5
5282.0941(10)	0.000 73	5155.8856(08)	−0.000 31	2_{12}	7	1_{11}	5
5287.4296(04)	−0.000 29	5160.0832(07)	−0.000 75	2_{12}	3	1_{11}	1
5295.7027(46)	−0.003 37	5166.6034(13)	−0.000 44	2_{12}	1	1_{11}	1
5582.4835(03)	0.000 05	5446.1835(12)	0.000 11	2_{02}	3	1_{01}	1
5584.0534(05)	−0.000 38	5447.4203(14)	−0.000 05	2_{02}	5	1_{01}	5
5596.7503(07)	−0.001 71	-	-	2_{02}	3	1_{01}	5
5600.1597(13)	0.000 96	5460.1265(15)	0.000 22	2_{02}	1	1_{01}	1
5601.7619(06)	0.001 75	5461.3859(11)	0.002 87	2_{02}	7	1_{01}	5
5601.8502(45)	0.001 66	5461.4467(12)	−0.000 93	2_{02}	5	1_{01}	3
5614.5469(07)	0.000 13	5471.4538(15)	0.000 45	2_{02}	3	1_{01}	3
5632.2222(12)	0.000 14	5485.3960(15)	−0.000 24	2_{02}	1	1_{01}	3
5950.6527(03)	0.001 31	5794.3849(09)	0.001 72	2_{11}	5	1_{10}	3
5957.4801(10)	0.000 46	5799.7651(17)	0.000 77	2_{11}	3	1_{10}	3
5958.8981(03)	0.000 79	5800.8850(10)	0.001 20	2_{11}	5	1_{10}	5
5965.7252(17)	−0.000 37	5806.2648(37)	−0.000 15	2_{11}	3	1_{10}	5
5967.0602(06)	−0.000 05	5807.3120(26)	0.000 75	2_{11}	1	1_{10}	3
5968.4276(20)	0.003 42	5808.3992(10)	0.002 71	2_{11}	7	1_{10}	5
5972.3443(14)	0.001 61	5811.4799(17)	0.001 55	2_{11}	3	1_{10}	1
5981.9242(04)	0.000 90	5819.0248(12)	−0.000 48	2_{11}	1	1_{10}	1

strengths eQq_{aa}, $eQq_{bb}-eQq_{cc}$, and eQq_{ab}. For inclusion of the off-diagonal quadrupole tensor element eQq_{ab}, it was necessary to use the fitting programs written by Pickett[9] and co-workers in all data analyses. A total of 63 lines were included in the fits, 35 for ^{79}Br- and 28 for ^{81}Br-ferrocene. Standard deviations for fits to the measured transitions were less than 3 kHz. The values of the parameters obtained are listed in Table VI. Only three measured lines were not included in these fits. These transitions may have been due to Q branches or other isotopomers. The off-diagonal element in the quadrupole coupling tensor was required for a satisfactory fit to the data. Exclusion of this parameter from the fit (setting $eQq_{ab}=0.0$ MHz) increased the standard devia-

tions to above 200 kHz. This parameter was not required to obtain reasonably good fits in the previous analyses of chloroferrocene data,[3] but more consistent results are obtained when it is included. The distortion constants for bromoferrocene were found to be small and no effects of internal rotation were observed, in agreement with the previously observed rigidity of chloroferrocene.

Structural parameters were determined from the six available rotational constants in a four parameter least squares fit with the following assumptions: 1) The carbon rings are assumed to be coplanar. 2) Local C_5 symmetry was assumed for the carbon and hydrogen atoms. 3) The C–H bond length was fixed at 1.08 Å. 4) The angle of the C–H

TABLE VI. Molecular parameters for the two isotopomers of bromoferrocene and new parameters for chloroferrocene using an estimated value for eQq_{ab}. Listed uncertainties are 2σ.

Parameter		^{79}Br	^{81}Br	^{35}Cl	^{37}Cl
A	(MHz)	1272.110(1)	1271.045(4)	1370.001(2)	1361.979(3)
B	(MHz)	516.1125(2)	510.0079(2)	767.3404(2)	751.5366(3)
C	(MHz)	441.3775(2)	436.7687(2)	634.8842(1)	622.3540(2)
D_{JK}	(kHz)	0.29(2)	0.26(36)	0.11(1)	0.11(2)
D_J	(kHz)	0.029(1)	0.021(2)	0.033(1)	0.034(2)
eQq_{aa}	(MHz)	267.16(3)	225.40(6)	−8.974(7)	−8.67(1)
$eQq_{bb}-eQq_{cc}$	(MHz)	310.15(4)	256.70(3)	−65.79(5)	−50.26(2)
eQq_{ab}	(MHz)	−409.81(4)	−341.62(4)	53.42[a]	42.42[a]
σ	(kHz)	2.8	1.1	2.9	2.9

[a]These values were fixed, see text for discussion.

TABLE VII. Structural parameters for chloroferrocene and bromoferrocene. Listed uncertainties are 2σ. The last row contains standard deviations for the fits, denoted by σ.

Parameter		X=Br	X=Cl
Fe–Cp	(Å)	1.63(2)	1.610(5)
Fe–CpX	(Å)	1.67(3)	1.693(2)
C–C	(Å)	1.433(1)	1.4332(2)
C–X	(Å)	1.875(11)	1.705(4)
σ	(kHz)	12	26

FIG. 1. Axis systems for the haloferrocenes. The c, u, and x axes are parallel to each other and are perpendicular to the page. The principal inertial axes are the a, b, and c axes, the principal quadrupole axes are the u, v, and w axes, and the C–X(X=Cl,Br) bond axes are the x, y, z axes.

bond to the carbon plane (designated as the C_5–H angle) was fixed at 4.6°, the value found for the gas-phase structure of ferrocene using gas-phase electron diffraction (GED) methods.[2] 5) The bromine atom is assumed to be in the plane of the five carbon atoms of the Cp group. The four parameters necessary to describe the structure of bromoferrocene after these assumptions are made are the Fe–Cp perpendicular distance, the Fe–CpBr perpendicular distance, the C–C bond length, and the C–Br bond length. The analogous analysis of the structure for chloroferrocene indicated a correlation between the angle of the hydrogen atoms with respect to the C_5 plane and the Fe–CpX (X=H,Cl) parameters, and therefore, this angle was fixed at the value determined from the GED analyses. Since no deuterated isotopomers of bromoferrocene were measured in this study, the same assumption was made for the angle between the C–H bonds, and the C_5 carbon plane.

The fit to determine the structural parameters using the rotational constants yielded standard deviations of only 12 kHz for bromoferrocene and 26 kHz for chloroferrocene (Table VII). However, changes in the symmetry assumptions or values of the assumed parameters would be likely to introduce larger error contributions than those given in Table VII. The uncertainty in the C_5–H angle is quite large, and this would contribute to propagated errors in the Fe–Cp and Fe–CpX distances. The errors given for the listed structural parameters include the propagated errors from the value of the C_5–H angle, whenever this propagated error exceeded 2σ from the structure fit. The structural parameters obtained are listed in Table VII.

Chloroferrocene

Previous work on chloroferrocene produced accurate structural results, but the analysis of the quadrupole coupling was hindered by the lack of data for the off-diagonal parameter, eQq_{ab}. Matrix rotation of approximate quadrupole coupling parameters from the bond axes into the inertial axes showed this term is likely to be small (less than 60 MHz) in comparison with the rotational constants. The off-diagonal elements only contribute small perturbations to the energy levels. Therefore, neglect of this parameter was not expected to introduce much error into the data analyses. However, values of the quadrupole coupling components in the bond axis system reported previously showed disagreement between quadrupole asymmetry parameters (η) obtained for different Cl isotopes. This was an indication of two prob-

lems: 1) The bond axis system was not aligned with the principal quadrupole axes of the electric field gradient, and therefore, the assumption that these two axes were aligned was not entirely valid; and 2) the off-diagonal quadrupole parameter was assumed to negligible. In order to improve the analysis, it was necessary to estimate a reasonably accurate value for the off-diagonal element eQq_{ab}. Due to the small value of eQq_{ab}, and the relatively small effect it has on the spectrum, it was not accurately determinable from a least squares fitting analysis of the spectra. This off-diagonal parameter was weakly correlated with the other quadrupole terms and the distortion constants, and it changed considerably when lines were added or subtracted from the fit. It seemed necessary to estimate a reasonable value of this parameter, eQq_{ab}, in order to accurately determine the seven remaining parameters. This off-diagonal term was estimated using the structurally determined angle Θ_s, the angle be-
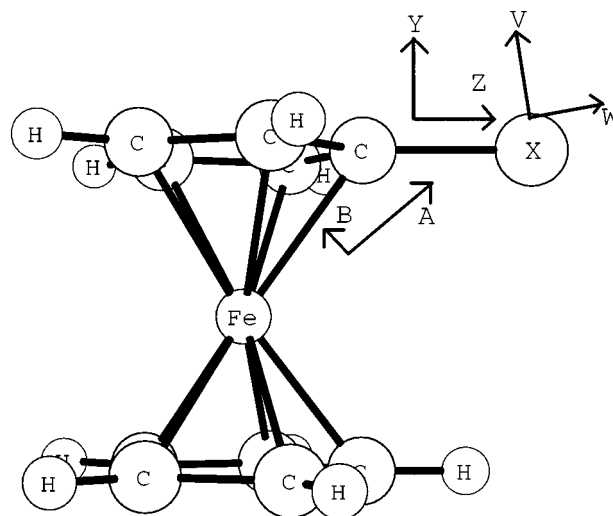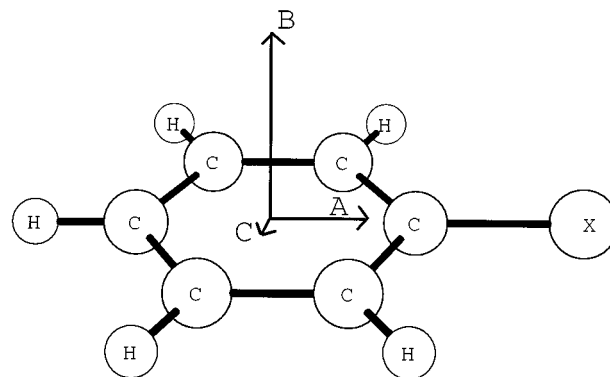
FIG. 2. The halobenzene C–X(X=Cl,Br) bond axis is parallel to the "a" inertial axis. For direct comparison with the bond axes of the haloferrocenes, the halobenzene a, b, and c axes correspond to the z, y, and x axes of the haloferrocenes, respectively.

TABLE VIII. Quadrupole coupling parameters for Cl- ferrocene and Br-ferrocene in the principal inertial axes (abc), the principle quadrupole axes (uvw) and the C–X bond axes (xyz) systems. Values for Cl-benzene and Br-benzene are included (last three rows) for comparison with the xyz and uvw components of the haloferrocenes.

		^{79}Br	^{81}Br	^{35}Cl	^{37}Cl
eQq_{aa}	(MHz)	267.16(3)	225.40(6)	−8.974(4)	−8.67(1)
eQq_{ab}	(MHz)	−409.81(4)	−341.62(4)	53.42	42.42
eQq_{bb}	(MHz)	21.49(4)	15.65(4)	−28.41(5)	−20.80(6)
$eQq_{cc}=eQq_{uu}=eQq_{xx}$	(MHz)	−288.66(4)	−241.05(4)	37.38(5)	29.47(6)
eQq_{vv}	(MHz)	−283.49	−236.83	35.61	28.12
eQq_{ww}	(MHz)	572.15	477.88	−72.98	−57.59
Θ_D	(°)	36.7[a]	36.5[a]	50.2[a]	49.1[a]
Θ_S	(°)	38.7[b]	38.5[b]	51.8[b]	50.7[b]
eQq_{yy}	(MHz)	−282.38	−235.91	35.52	28.05
eQq_{yz}	(MHz)	30.85	25.66	−3.08	−2.47
eQq_{zz}	(MHz)	571.03	476.95	−72.89	−57.52
$\eta(CpFeC_5H_4X)$		−0.011	−0.011	−0.025	−0.025
eQq_{aa} (C_6H_5X)	(MHz)	558.9(13)	464.1(18)	−71.234(1)	−56.144(1)
eQq_{bb} (C_6H_5X)	(MHz)	−292.5(5)	−242.7(7)	38.215(3)	30.120(3)
$\eta(C_6H_5X)$		−0.046(4)	−0.046(7)	−0.07296(3)	−0.07295(4)

[a]This angle represents the matrix rotation angle necessary for diagonalization of the 2×2 block matrix of the quadrupole parameters along the a and b axes. The u, v, and w axes correspond most directly with the x, y, and z axes, respectively. The a and b axes of the halobenzenes correspond to the z and x axes of the haloferrocenes.

[b]These angles were determined from the structural parameters via rotation from the fixed (abc) system into the desired (xyz) coordinate system.

tween the a and z axes, and the relation between the quadrupole coupling tensor elements (primarily η) of chlorobenzene. The parameters obtained from this revised analysis, with some new data, are given in Table VI.

The quadrupole coupling tensors obtained for bromoferrocene, chloroferrocene, bromobenzene, and chlorobenzene, in various axis systems, are shown in Table VIII. The axes are shown in Figs. 1 and 2. Comparison of the bromoferrocene quadrupole coupling constants in the bond axis system with those of bromobenzene[10] show remarkable agreement. The similarity between the C–Br bond in the two ring systems produces quadrupole coupling parameters within 5% of each other. Accurate values for the rotated quadrupole coupling tensor could be obtained because the off-diagonal term in the bond axis system was well determined in the bromoferrocene spectral fit. The chloroferrocene quadrupole coupling tensor is approximately one order of magnitude smaller than that of bromoferrocene, and therefore, the contribution of the off-diagonal terms in the quadrupole coupling tensor are considerably smaller. This made the parameter eQq_{ab} quite difficult to accurately determine from the spectrum of chloroferrocene (*see above*). Based on reasonable agreement between the quadrupole coupling terms in bromobenzene and bromoferrocene, a value for this parameter in chloroferrocene was estimated, based on quadrupole coupling in chlorobenzene (Refs. 7, 8, and present analysis) and the previously determined angle Θ_s. In this analysis, it is assumed that the C–Cl bond-axis quadrupole coupling tensor in chloroferrocene is very similar to the C–Cl bond-axis quadrupole coupling tensor for chlorobenzene. The axis systems for the halobenzenes are shown in Fig. 2. From the analysis of bromoferrocene, one would expect that there

would be a residual off-diagonal element in the xyz bond axis system due to the slight misalignment of the bond axes with the principal quadrupole axes. This off-diagonal term in the bond axis systems is expected to be small because the principal quadrupole axis systems and the bond axis systems are only slightly misaligned, and all quadrupole coupling elements are much smaller for chloroferrocene. For comparison purposes, the principal quadrupole coupling tensors and the bond axes quadrupole coupling tensors can be calculated after the value of eQq_{ab} is assumed, but the accuracy of these values will reflect the errors in this model (estimated to be about 10%).

Analyses of quadrupole coupling in the bond axis systems of both haloferrocenes required determination of the angle of rotation from the abc (inertial) axes to the xyz (bond) axes. This angle was determined from the structural parameters after transformation to the center of mass frame from the xyz frame using the following matrix rotation,

$$\begin{pmatrix} \cos \Theta & -\sin \Theta_s & 0 \\ \sin \Theta_s & \cos \Theta_s & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} z \\ y \\ x \end{pmatrix} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}.$$

The column vectors in this expression represent the coordinates of an atom in the xyz and abc systems, and the rotation matrix provides the corresponding vector transformation. See Fig. 1 for an illustration of these axes. The angle between the ''z'' and ''a'' axes is Θ_s. This angle depends only on the molecular structure of the given isotopomer and the assumptions made in the structure fitting process. For the ^{35}Cl and ^{37}Cl isotopomers, it was determined to be 51.8(3)°

TABLE IX. Molecular parameters for ^{35}Cl- and ^{37}Cl-benzene obtained by fitting the spectra.

Parameter		^{35}Cl	^{37}Cl
A	(MHz)	5672.43(9)	5672.5(1)
B	(MHz)	1576.784 33(8)	1532.786 27(8)
C	(MHz)	1233.675 71(5)	1206.575 56(6)
eQq_{aa}	(MHz)	$-71.234(1)$	$-56.144(1)$
$eQq_{bb}-eQq_{cc}$	(MHz)	5.197(4)	4.095(4)
σ	(kHz)	1.5	1.7

and 50.7(3)°, respectively; for the ^{79}Br and ^{81}Br isotopomers, it was determined to be 36.7(3)° and 36.5(3)°, respectively.

The quadrupole coupling in chlorobenzene had been previously studied in detail for the main isotopomer ^{35}Cl using a traditional waveguide microwave spectrometer,[7,8] so the accuracy and precision of the quadrupole coupling parameters were not very high. For proper estimation of the off-diagonal elements in chloroferrocene, better information on both isotopomers was required. About 25 lines were measured for each isotopomer, and they are given in Table V. The results of fitting this data are given in Table IX. The parameter values are in agreement with previously published results.[7,8]

In order to estimate eQq_{ab}, the values of eQq_{aa} and eQq_{bb} determined from the chlorobenzene data were placed in the xyz (C–Cl) bond axis frame of chloroferrocene and then rotated into the abc axes of chloroferrocene using the angle Θ_S, and the following transformation:

$$
\begin{pmatrix} \cos\Theta_s & \sin\Theta_s & 0 \\ -\sin\Theta_s & \cos\Theta_s & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} eQq_{zz} & 0 & 0 \\ 0 & eQq_{yy} & 0 \\ 0 & 0 & eQq_{xx} \end{pmatrix}
$$

$$
\times \begin{pmatrix} \cos\Theta_s & -\sin\Theta_s & 0 \\ \sin\Theta_s & \cos\Theta_s & 0 \\ 0 & 0 & 1 \end{pmatrix}
$$

$$
= \begin{pmatrix} eQq_{aa} & eQq_{ab} & 0 \\ eQq_{ab} & eQq_{bb} & 0 \\ 0 & 0 & eQq_{cc} \end{pmatrix}.
$$

The value of Θ_S in the rotation matrices was discussed previously. The starting xyz quadrupole tensor elements are the values measured for chlorobenzene, and the final tensor is the approximate chloroferrocene quadrupole coupling tensor in the principal inertial axis frame. The values for eQq_{ab} and eQq_{bb} were within 10% of the parameters determined in the eight parameter fits, but the eQq_{aa} values were not as accurate, due to the small magnitude of this parameter and the fact that it has a strong dependence on the rotation angle. Only the value of eQq_{ab} from these calculations was used in the new spectral fits. More consistent results were obtained using this procedure, with a fixed value for eQq_{ab}. Inclusion of this term into the spectral fit of chloroferrocene also allowed higher K states to be included in the fit, and so, additional lines were measured for inclusion in the analyses. Three lines from the previous spectral fit were reassigned to

different F values. The rotational constants determined in the new spectral fit are in excellent agreement with the previously published values, so the previously published structure is still considered to be valid. The distortion constants, D_J and D_{JK}, from the revised analyses are considerably different from the previously published values and are now in better agreement with each other and with those obtained for bromoferrocene.

CONCLUSIONS

The present paper describes the first molecular structure measurements for bromoferrocene and only the second structural study of a substituted ferrocene in the gas phase. The structural fit provided parameters for the molecular structure. Since data on only two isotopomers were obtained, the uncertainties in the structural parameters are fairly large. Without further study of deuterated and/or ^{13}C substituted isotopomers, the present structural assumptions are necessary in order to keep the number of variable parameters less than the number of measured rotational constants. As was observed for chloroferrocene, the substitution of an electronegative atom onto the ferrocene frame increases the metal to carbon bond length in comparison to ferrocene. The Fe–CpX distances for X=Br,Cl are in agreement, as are the C–C bond length and the Fe–Cp distances in the two haloferrocenes. The values determined for the C–X bond lengths are in excellent agreement with those of the halobenzenes, which are 1.712 and 1.8674 Å for r(C–Cl) and r(C–Br), respectively.[7,8,10]

The close agreement between the halobenzene and haloferrocene quadrupole coupling tensors was not expected. Bonding of the Cp carbon atoms to iron certainly must perturb the electronic charge distribution around the carbon atoms, but apparently does not have a large effect on the electric field gradients at the halogen atom. The principal axis system for the electric field gradient is only rotated 1–2° out of the Cp plane due to bonding to the iron atom. For comparison to previous results published on chloroferrocene, chlorobenzene, and bromobenzene, the data from chloroferrocene were reanalyzed using the same fitting routines and variable parameters as used with the new bromoferrocene data. For the halobenzenes, the principal quadrupole axes are aligned with the bond axes, and also the inertial axes, due to their C_{2v} symmetry. With this symmetry requirement, there will be no expected off-diagonal quadrupole coupling terms, and the principal inertial axes of the molecule coincide with the bond axes. However, the haloferrocene inertial axes are significantly different from the C–X bond axes and are not necessarily aligned with the principal quadrupole axes due to perturbation of the electric field gradients by the iron atom (and the other Cp group). Therefore, there are three separate axis systems to be considered when describing the quadrupole coupling in a haloferrocene. The values of the quadrupole coupling parameters, along these various axes, are shown in Table VIII, along with the parameters for the corresponding halobenzenes. The first three listed values are the quadrupole coupling parameters along the abc inertial axes

that are determined directly from the values from the spectral fit. The third term, eQq_{cc}, is invariant to rotation of the molecule about the ''c'' axis. Therefore, this term is the same in both systems and will correspond to the value along the x axis, which is perpendicular to the C–Br bond and in the plane of the Cp group. Furthermore, the ''u'' axis of the principal quadrupole axis system will be parallel to the ''c'' and ''x'' axes. The bromine atom lies in the ab plane, and therefore, isotopic substitution does not rotate the c axis. This allows an accurate and direct determination of the nuclear quadrupole moment ratio. For bromoferrocene this value was determined to be $eQq_{cc}(^{79}Br)/eQq_{cc}(^{81}Br) = 1.1975(18)$. This ratio is in good agreement with previous values of 1.1968 for CH_3Br,[11] and 1.197 057 for atomic bromine.[12]

The quadrupole coupling values in the xyz bond axis system were determined by rotating the abc quadrupole coupling tensor by Θ_S. The remaining, nonzero, off-diagonal parameter, eQq_{yz}, is an indication of a misalignment between the bond axes and the principal quadrupole tensor axes. One method for determination of the angle between the xyz and uvw axes is by direct diagonalization of the quadrupole tensor in the xyz bond axis system. This method gives 1.6(3)° for both of the chlorine isotopomers and 2.0(3)° for both of the bromine isotopomers. Another method used involves direct diagonalization of the abc quadrupole coupling tensors, then the structurally determined angle listed above is subtracted from the angle of rotation found in this diagonalization process. The results of the two methods are in agreement.

Interpretation of the quadrupole coupling parameters in the xyz coordinate system shows that the halogen electric field gradients in the haloferrocenes are very similar to the analogous field gradients in the halobenzenes. The small angle of rotation of the principal axis system out of the bond axis system indicates that the presence of the η^5 metal–carbon bonding only slightly perturbs the electronic structure of the C–X bond.

ACKNOWLEDGMENTS

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