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The Carbonyliron Complexes of Some Chlorocarbons

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The (tetracarbonyl)iron complexes of perchloro-(3,4-dimethylenecyclobutene) and perchlorofulvene, and the (tricarbonyl)iron complex of the former chlorocarbon were synthesized. The structural evidences for those complexes were given on the basis of the DSC, their chemical behaviors, and the UV, IR and other spectral data. Particularly, their mass-, NQR- and ^{13}C-NMR-spectra were discussed in detail by comparing them with those of the substrate chlorocarbons.

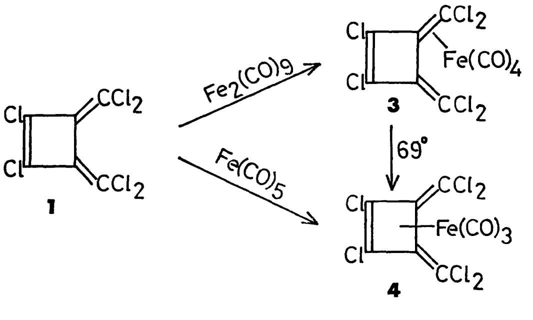
Little has been reported on the carbonyliron complexes with chlorocarbons as organic ligand. The thermochemical stabilities of a number of $L\cdot Fe(CO)_4$ type complexes (L: substituted ethylene) were discussed from the MO theoretical point of view by correlating their V-[1] or D/A- values[2] respectively with the ν_{CO} frequencies or the force constants in IR spectroscopy. However, the highly retarded chemical reactivity of conjugated polyenic chlorocarbons may have been a barrier to promote the work in this field; for instance, tetrachloroethylene, the simplest olefinic chlorocarbon, reacts with nonacarbonyl diiron under ordinary conditions to give the complex, but only in 0.1% yield,[3] reflecting a severe effect of perchloro-substitution. To our present knowledge, no carbonyliron compounds complexed with other chlorocarbon have appeared in the literature.

We examined the reactions between pentacarbonyl iron or nonacarbonyl diiron and three cyclic C_6Cl_6 chlorocarbons; *i.e.*, perchloro-(3,4-dimethylenecyclobutene) (**1**), -fulvene (**2**) and -benzene. Two kinds of complexes with the types of $L\cdot Fe(CO)_4$ and $L\cdot Fe(CO)_3$ were obtained from **1**, whereas only the one with the former type from **2**. Perchlorobenzene did not react with the reagents at all.

This paper describes the syntheses and some degradative reactions of those complexes, and discusses their structures mainly in terms of the IR-, mass-, NQR- and ^{13}C-NMR spectral data.

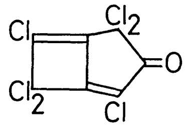
Results and Discussion

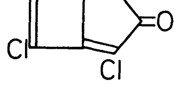
Syntheses and Degradative Reactions of Carbonyliron Complexes with Chlorocarbon Ligand. The chlorocarbon **1** reacted with nonacarbonyl diiron under the conditions specified in the experimental to furnish a complex (**3**), $C_6Cl_6Fe(CO)_4$ (mp 47.0 °C and decomp. *ca.* 76 °C, from the DSC). The oxidative degradation with Fe(III) or Ce(IV) smoothly liberated **1**. The thermal decomposition near 65 °C also proved the liberation of **1**, but there was no indication that dodecacarbonyl triiron formed through the trimerization of the component. The UV absorption for **3** were: $\lambda_{\max}^{n\text{-hexane}}$ 230 (4.43), 287 (4.30) nm (log ε).



1 **3** **4**

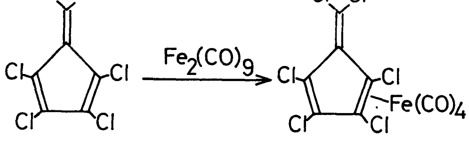
The second complex (**4**), $C_6Cl_6Fe(CO)_3$ (mp and dp: 90.5 and 105 °C, respectively, by DSC) was obtained by refluxing **3** in *n*-hexane with the inevitable production of **1**. The pyrolytic or oxidative liberation of **1** was essentially parallel to the above. Very drastic change in the UV spectrum ($\lambda_{\max}^{n\text{-hexane}}$ 215 (4.36), 260_{sh} (3.99), 310_{sh} (3.70) and 386 (3.39); nm (log ε)) was observed in **4**. The only characteristically different behavior of **4** was the byproduction of a ketone (**5**) (mp 117 °C), C_7Cl_6O in the pyrolysis. The structure of perchloro-(bicyclo[3.2.0]hepta-1,5-diene-3-one) (**5a**) or its 1,6-diene alternative (**5b**) was assigned to **5** mainly on the basis of the UV spectral data.


5a


5b

The complex **4** was also produced by heating **1** and pentacarbonyl iron in a sealed tube at 85 °C, but in a poor yield.

The chlorocarbon **2** afforded in the analogous way the complex (**6**), $C_6Cl_6Fe(CO)_4$, through the reaction with nonacarbonyl diiron. The liberation of the substrate by either pyrolysis or the oxidative degradation was also confirmed. The observed mp by DSC was 72 °C. Interestingly, the exothermic degradation pattern of **6** suggested a two step successive loss of carbon monoxide, one at 84.5 °C, and the rest three at 93.5 °C.



2 **6**

Further attempt was made to prepare the complex of *h*^{4}-type starting with **6** by the pyrolysis in *n*-hexane. Unfortunately, however, the product was too unstable to be well caracterized; even very careful purification by chromatography near 0 °C resulted in failure in isolating the complex pure enough for succeeding analysis.

No formation of binuclear complex were observed in all the reactions of this work.

*IR Spectra** It was expected from the calculated HOMOs (by EHT) and the observed $\pi \rightarrow \pi^*$ energies of the chlorocarbons (−10.38 and 5.14 eV for **1** and −10.49 and 4.13 eV for **2**, respectively), that their interaction with $Fe(CO)_4$ (ionization potential: 7.0 eV[4]) would be much more advantageous for the complex formation than those in this case of dichloroethylenes (*e.g.*, for *trans*-isomer: HOMO −9.72 eV, $\pi \rightarrow \pi^*$ 6.49 eV[2]). There would be an effective stabilization in the total energy due to the back-donative bond formation.

The IR spectra of **3** gave rise to four very strong ν_{CO} bands at 2120, 2075, 2060 and 2035 cm^{-1}, indicative of the contribution of this back-donation from the central atom to the ligand, as well as of the equatorial position[5] of the latter in a trigonal bipyramidal structure. The band with the highest wave number and the lowest intensity due to A_1 asymmetric stretching vibration fell into the range between that for C_2Cl_4–$Fe(CO)_4$ (2134 cm^{-1}, the highest ever reported)[3] and those for 1,2-dichloroethylene-complexes (2106 cm^{-1})[2]. The $\nu_{C=C}$ bands corresponding to the free double bonds were at 1652 and 1595 cm^{-1}. An additional very weak band at 1375 cm^{-1} was detected by the special examination with a thick perchlorobutadiene mull; this should correspond to the double bond coordinated by the central atom. There have been no reports that describe such a drastic $\nu_{C=C}$ shift, but the $\Delta\nu_{C=C}$ value of *ca.* 170 cm^{-1} was within the acceptable range.[5]

The observed ν_{CO} bands of **4** were 2105 (vs) and 2065 (vs and broad) cm^{-1}, typical for diene–(tricarbonyl)iron complex.[6] The highest band was 52 cm^{-1} higher than the corresponding one of butadiene–$Fe(CO)_3$,[7] and will be the highest of all on reports as for the h^4-type complexes except some with cationic ligand.[8] Two strong $\nu_{C=C}$ bands with almost equal intensity were observed; the one at 1676 cm^{-1} for the free double bond and the other at 1375 cm^{-1} for the metal-coordinated.

The ν_{CO} bands (2120, 2070, 2065 and 2040 cm^{-1}, all vs) of **6** were almost the same as those for **3**. Therefore, the position of the organic ligand in the complex was assigned also to be equatorial in a trigonal bipyramidal structure, and the back-donation was nearly of the same extent. The $\nu_{C=C}$ bands appeared as two peaks (1570 and 1530 cm^{-1}, both s) splitted from the single broad one (1568 cm^{-1}, s) in **2**, and interestingly in this case, no band for the shifted $\nu_{C=C}$ was observed in the region 1500—1300 cm^{-1} even with a highly concentrated perchlorobutadiene solution.

Mass Spectra. The relative abundances are listed in Table 1 only for the main fragments including metal and/or C_6-skeleton from **1**, **2**, **3**, **4** and **6**. The distributions for the species less than C_5 were in all cases rather random and did not seem so informative. The successive loss of chlorine atom below *m/e* 282 in the cracking pattern was typically observed for all.

TABLE 1. RELATIVE ABUNDANCE IN THE MASS SPECTRA OF **1**, **2**, **3**, **4** AND **6**

m/e[a)]	Ions	**1**	**2**[b)]	**3**[c)]	**4**	**6**
422	$C_6Cl_6\ Fe(CO)_x^+$ (x=3—0)	—	—	8	9	0
394				10	10	0
366				11	8	0
338				23	21	0
282	$C_6Cl_6^+$	77	100 (100)	42	5	100
247	$C_6Cl_5^+$	100	40 (39)	63	12	63
212	$C_6Cl_4^+$	33	21 (23)	100	100	30
177	$C_6Cl_3^+$	11	7	53	40	21
168	$Fe(CO)_4^+$	—	—	7	0	2
142	$C_6Cl_2^+$	23	17	84	67	49
140	$Fe(CO)_3^+$	—	—	9	0	0
126	$FeCl_2^+$	—	—	5	5	0
112	$Fe(CO)_2^+$	—	—	15	3	0
107	C_6Cl^+	11	10	28	20	54
91	$FeCl^+$	—	—	25	32	6
84	$Fe(CO)^+$	—	—	25	9	21

a) The *m/e*s are arranged monoisotopically, but their relative abundances are of all isotopic variants. b) Values in parentheses are from Ref. 9. c) Very poor production for *m/e* 450 (x=4).

However, some special comments can be made on the following points.

1) The cracking patterns are markedly different between **1** and **2** only in terms of the ratios of the relative abundance ($C_6Cl_6^+/C_6Cl_5^+$), although the distributions of other ions C_6Cl_x (x=3 or less) are essentially the same. Since the data for **2** meet well those reported by Meyerson *et al.*,[9] we suspect their suggestion that the cationized **1** would be the most possible intermediate fragment of perchloro-(1,2-dimethylenecyclobutane).

2) It was observed that the complex formation from **1** makes the fragmentation to C_6Cl_x (x=5 or less) dominant. This trend is rather common between **3** and **4**, and can be explained by the dominant elimination of FeCl or $FeCl_2$ from $C_6Cl_6Fe^+$ (*m/e* 338); the former elimination was evidenced by the relatively high abundance of the ion (*m/e* 91). The very small value for $C_6Cl_6^+$ from **4** seems to be related with the increased value for $FeCl^+$ ion, and further with the stability of L–Fe linkage in **4**.

3) On the other hand, **6** degradates under the same conditions quite differently; no $C_6Cl_6Fe(CO)_x^+$ fragments (x=4—0) were observed, and corresponding to this, the relative abundance of $FeCl^+$ was very small. The first fission of the L–Fe bond by electron impact must be the most essential fragmentation process in this case.

NQR Spectra. The NQR was particularly useful when, as our case, the direct comparison of the data between the ligand- and substrate-chlorocarbon is possible. The resonance lines for **1**, **3** and **4** are shown in Fig. 1, where the numerical figures indicate the values obtained by extrapolating the temperature dependence curve to 0 K for simpler and more precise

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* Measured in C_2Cl_4 solution unless otherwise noted.

representation. It was generally experienced that the complex formation causes the intensification of the signals so effectively that the strong lines do appear even at room temperature. In all cases the number of crystallographically inequivalent chlorine atoms were found to be six.

It can be seen in Fig. 1 that some systematic frequency shifts exist through complex formation from **1**. The middle two lines for **3** near 37.5 MHz probably correspond to the two of four lines for **1** in the 38.0 MHz region which have already been assigned to the chlorine atoms at the exocyclic methylene carbons in the molecule.[10] Hence, the carbonyl iron-group presumably makes the π-bond with one of these double bond moieties, lowering the resonance frequencies for the chlorines attached to C_3', or C_4' of **1**. Another feature of the spectrum for **3** was the shifts of one of the two lines near 36.5 MHz assigned to the ring chlorines[10] to the higher frequency region, either because of the crystal field effect,** or as the result of some minor spatial interaction with one of the axial carbonyl groups. These interpretations may constitute the most principal reason for giving the structure of *acde*-tetracarbonyl-*b*-{1-1'-η-perchloro-(3,4-dimethylenecyclobutene)} iron finally to **3**.

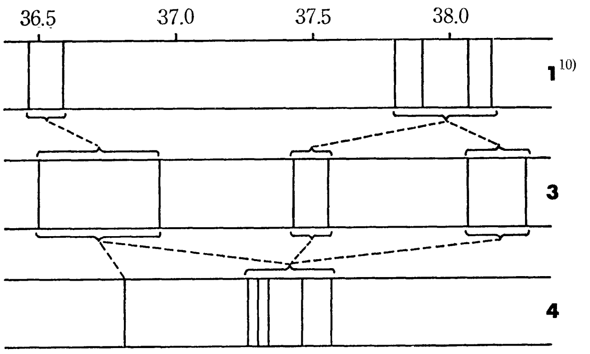

Fig. 1. NQR lines for **1**, **3**, and **4**.

In the resonance line pattern for **4**, the rest two lines with the highest frequency values also shifted downward joining together with the middle two for **3**. This suggests that the carbonyl iron interacts with both of the exocyclic double bonds of the ligand. In the 37.5 MHz region were observed actually five lines, one of which is obviously assigned to the chlorine atom on the four-membered ring. The upward shift is perhaps attributed to the spatial effect of the carbonyl group, deviating to some extent from the σ_v of the ligand, and hence, resulting in the lack of C_s symmetry of the complex molecule as a whole. The lowering of the resonance frequency caused by metal coordination is due to the releasing of the Cl-p_x electron through pi-conjugation according to the equation:[12]

$$fq \propto (N_x+N_y)/2 - N_z,$$

where N_x, N_y and N_z are the 3p AO population of a chlorine atom in x-, y- and z(C-Cl)-direction, respec-

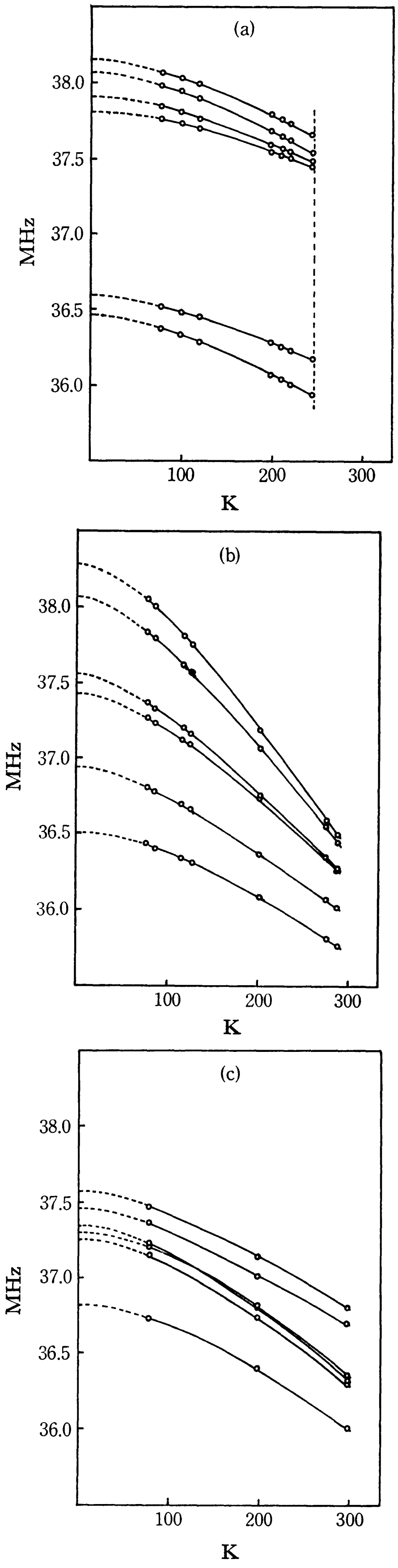

Fig. 2. Temperature dependences of NQR lines for **1**, **3**, and **4**. The vertical broken line in 2(a) indicates the fade-out temperature

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** The frequency shifts seem more than those due to the crystal field effect which has been estimated to be less than 500 KHz in ordinary cases.[11]

tively. Thus, the structure of tricarbonyl-{1′-2′-η-perchloro-(3,4-dimethylenecyclobutene)}iron was assigned to **4**, although its stereochemical configuration has remained unsolved.

In order to see more detailed profile of the complexes in terms of the thermal molecular motion in crystals, the temperature dependence of those NQR lines were examined (Table 2 and Fig. 2). The fade-out of all six signals for **1** at 250 K or so (Fig. 2a) and the survival of the six strong ones for both **3** and **4** even at room temperature (Fig. 2b and 2c) may be a reflection of the situation that the complex formation is sensitively related to some restricted thermal molecular motion. The most salient feature among the Figs. 2a—c is the extraordinarily large temperature gradients of the curves in Fig. 2b for the signals ν_1 and ν_2 assigned to the chlorines at the exocyclic double bond moiety free from the coordination. The high steepness of the curves suggests that those two chlorines both become more affected locally than others by the thermal motion of the nearest carbonyl group as the temperature rises. This interpretation is also helpful for understanding the existence of the valence isomerization in **3**, about which a comment will be given later. The curves for **4** are all as easy as those for **1** making a clear contrast to that for **3**.

TABLE 2. TEMPERATURE DEPENDENCE OF NQR LINES (MHz)

Temp. (K)		ν_1	ν_2	ν_3	ν_4	ν_4	ν_6
3	0	38.28	38.07	37.56	37.43	36.94	36.50
	78	38.052	37.829	37.362	37.257	36.800	36.426
	200	37.190	37.070	36.760	36.732	36.350	36.090
	286	36.504	36.439	36.264	36.247	36.011	35.758
4	0	37.57	37.46	37.34	37.30	37.26	36.81
	78	37.461	37.362	37.223	37.198	37.145	36.733
	198	37.146	37.048	36.812	36.802	36.740	36.410
	298	36.803	36.705	36.366	36.324	36.308	36.042
6	0	38.21	38.07	37.80	37.63	37.60	36.41
	78	38.150	37.988	37.742	37.555	37.533	36.341
	198	37.939	37.639	37.478	37.239	37.200	36.027
	298	37.683	37.247	37.093	36.883	36.825	35.689

Figure 3 shows the resonance lines for **2** and **6**. Some published informations on the structural problem for **2** are available; *e.g.*, the phase transition between the ordered and the disordered forms studied by X-ray analysis,[13] two mutually different NQR assignments,[10,14] *etc.* Even on these backround, however, it appeared very difficult to find some systematic shift of the lines in this case. The slopes of the temperature dependence (Table 2 and Fig. 5) are somewhat easier than those for **2** and **4**.

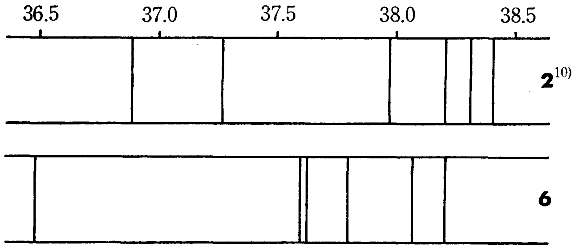


Fig. 3. NQR lines for **2** and **6**.

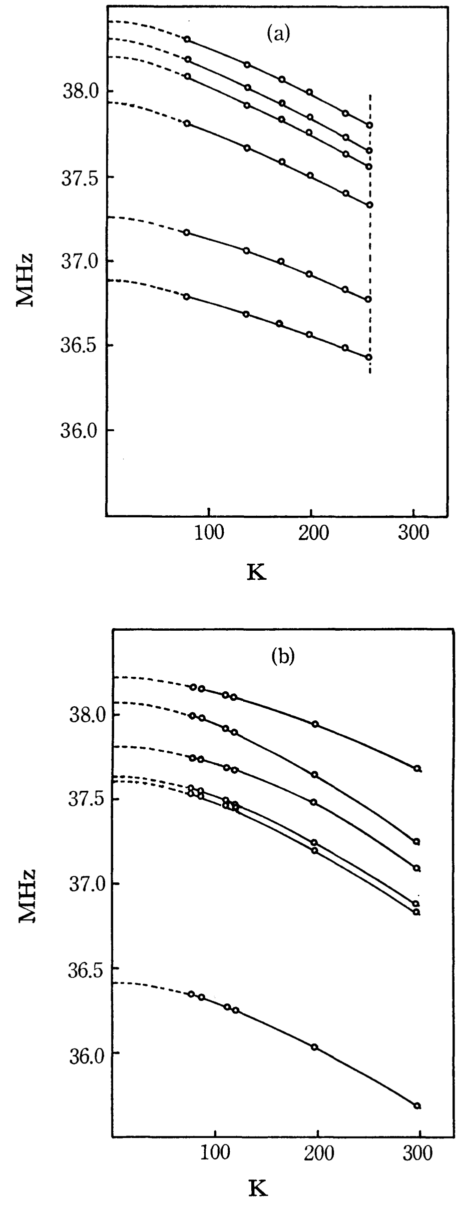


Fig. 4. Temperature dependences of NQR lines for **2** and **6**. The vertical broken line in 4(a) indicates the fade-out temperature.

The possible existence of phase transitions in those complexes were examined by means of DSC technique covering the low temperature range down to −160 °C. The observation of the inoccurence of such transition appeares parallel to our findings that the complex formation makes the molecular motion more restricted.

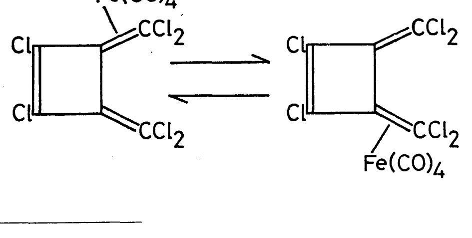
^{13}*C-NMR Spectra.* The ^{13}C-NMR spectra were taken for all the complexes and the substrate chlorocarbons. The FT-NMR measurement was accompanied by some technical difficulty because of the unstability of the complexes in solution, and, in addition, because of the extraordinarily long relaxation time of the excited species. However, successful results were obtained under the conditions specified in Table 3.

The reported data for ^{13}C-NMR of the carbonyliron complexes with hydrocarbon ligand inform, although they are very few, of a surprisingly large upfield shift for the signal related to the olefinic carbon coordinated by metal. In the case of butadiene–$\mathrm{Fe(CO)_3}$ complex, a pair of highly shifted signals, 35.8 and 80.8 ppm downfield from TMS was reported.[15] In our results, the signals in the 65—80 ppm region can be assigned also to the carbons coordinated by the iron metal. The absorption of the carbonyl-C in the complexes **3** and **6** are both very broad and splitted into two parts particularly in the former. The main reason for this broadening would presumably be either a very long relaxation of the carbonyl-C or the mutual transposition of the four carbonyls with an appropriately slow rate. Especially interesting was the appearence of only three signals in the complex **3**, which should give the six for ligand carbons, if the structure discussed in the preceding section is correct. The possibility that the carbonyliron positions at the double bond in the four-membered ring of **1** was certainly excluded from consideration on the basis of our present NQR interpretation. The most possible and rational explanation is the rapid degenerate rearrangement of **3** in the *d*-chloroform solution as shown below.*** The fluctional transposition of the bond between the iron and the C=C moiety may be related to the characteristically steeper temperature dependence curves in Fig. 2b. Some analogous examples have been dealt with in the carbonyliron complexes of allene,[17] cyclooctatetraene,[18] *etc.* The signal for the carbonyl-C of **4** was a sharp singlet and differed from those of **3** and **6**. No extraordinary upfield shifts for the olefinic carbons were observed in this case. This would be an exception with the potential significance that the h^4-type complex formation with chlorocarbon does not affect the absorption of the ligand so much as does the similar coordination in the hydrocarbon-complexes.

Table 3. ^{13}C-NMR chemical shifts for **1**, **2**, **3**, **4** and **6** (ppm downfield from TMS)

Compound	Carbonyl-C	Olefinic-C
1†		136.15, 131.66, 109.84
3	202.68, 202.41	139.39, 117.88, 73.91
4	199.23	149.23, 116.97, 105.98
2†		136.58, 130.87, 130.27 117.42
6	201.70	146.11, 142.61, 126.11 115.99, 76.27, 68.57

Solvent: $\mathrm{C_6D_6}$ for **4** and $\mathrm{CDCl_3}$ for others. Temperature: 0—10 °C for **3**, **4** and **6**; 40—50 °C for **1** and **2**. Approx. concentration: 2.5 g/5 ml (sample/solvent) for **3**, **4** and **6**; 1.5 g/5 ml for **1** and **2**. Pulse width: 1 μs. Pulse interval: 1.4 s. † See also Ref. 16.



The observation of seven signals in total for **6** (six for the olefinic-C and one for the carbonyl-C) explained the coordination of the central atom at 1,2- C=C bond of **2**. If the C=C bond at 5,5′ is coordinated, the number of signals for the ligand would be four. Thus, the structure of *acde*-tetracarbonyl-*b*-{1-2-η-perchloro-(5-methylenecyclopentadiene)}iron was assigned to **6**.

Experimental

The preparations and purifications of the complexes were all carried out under the atmosphere of nitrogen and with sufficiently deaerated solvent. Especially, the low temperature chromatography at 2—10 °C (on sillicic acid, Mallinkrodt, 100 mesh) was applied for the isolation.

The spectrometers used were JASCO-DS-402-G for IR, Hitachi EPS-2U for UV, Decca for NQR, JEOL-JMS D-100 and Hitachi RMU-6E for MS and Varian XL-100 for ^{13}C-NMR. For the NQR measurement a special rf-coil was designed for detecting signals with high sensitivity and a grid-dipmeter (Delica, Mita Musen Kenkyusho KK.) for checking the proper absorption frequencies were used. The DSC data were obtained by Rigaku DSC-8001.

*acde-Tetracarbonyl-*b*-{1-1′-η-perchloro-(3,4-dimethylenecyclobutene)}iron (3).* An *n*-hexane solution (200 ml) of perchloro-(3,4-dimethylenecyclobutene) (**1**) (4.0 g, 14 mmol) was stirred with nonacarbonyl diiron (6.2 g, 17 mmol) suspended in it, and gentle warming was applied until the temperature rose to 42 °C in 15 min, while the yellow suspension gradually changed to dark brown in color. The almost clear solution was obtained after 10 min keeping at 42—43 °C. The dark red solution obtained after cooling to room temperature and filtration through Hyflo Super-Cel (John-Manville) afforded, on removal of the solvent under reduced pressure below 30 °C, the crude crystals of the complex (**3**), which were purified by chromatography with *n*-hexane solution. The first fraction was composed of the recovered **1** (1.5 g). The lemon yellow crystals (4.3 g, 68%) of **3** were obtained as the second, and recrystallized from *n*-pentane at −78 °C. Found: C, 26.66; Cl, 47.31%. Calcd for $\mathrm{C_{10}Cl_6FeO_4}$: C, 26.50; Cl, 46.99%.

Tricarbonyl{1′-2′-η-perchloro-(3,4-dimethylenecyclobutene)}iron (4). The complex **3** (1.0 g, 2.2 mmol) was dissolved in *n*-hexane (65 ml) and the solution was heated under stirring so mildly that the solution started to reflux after 45 min. Being kept for several min under refluxing, the solution was cooled, filtered and chromatographed. The recovered **1** as the first fraction weighed 260 mg. The yellow crystals (150 mg) obtained as the second were recrystallized from *n*-pentane. Found: C, 25.35; Cl, 50.73%. Calcd for $\mathrm{C_9Cl_6FeO_3}$: C, 25.42; Cl, 50.14%.

*acde-Tetracarbonyl-*b*-{1-2-η-perchloro-(5-methylenecyclopentadiene)}iron (6).* To the solution of perchlorofulvene (**2**) (3.0 g, 10.5 mmol) in *n*-hexane (300 ml) was added nonacarbonyl diiron (3.9 g, 10.7 mmol) and the mixture was under stirring warmed gently for 1 hr until the temperature reached 40 °C, when the suspension of carbonyl iron disappeared within several min. The solution was cooled to room temperature and filtered through a glass filter. The regular work-up afforded the recovered **2** (0.4 g) and the orange

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*** An attempted measurement at the temperature lower than −40 °C was technically unsuccessful.

crystals of the complex (**6**) (2.0 g, 48%), which were recrystallized from *n*-pentane at −78 °C. Found: C, 26.67; Cl, 46.94%. Calcd for $C_{10}Cl_6FeO_4$: C, 26.50; Cl, 46.99%.

*Pyrolyses of the Complexes **3** and **6** to the Original Chlorocarbons.* The pyrolyses of **3** (64 mg) and **6** (74 mg) were carried out in the test tubes respectively at 65—66 °C for 2 min and at 85 °C for 10 min. The partial production of **1** was confirmed by the IR spectrum in the former case and that of **2** (24 mg) by the isolation of the latter.

*A Typical Example among the Oxidative Degradations of the Complexes **3**—**6** by Cerric Ammonium Nitrate.* The solution of **6** (340 mg) in acetone (30 ml) was stirred with cerric ammonium nitrate ($Ce(NO_3)_4 \cdot 2NH_4NO_3 \cdot xH_2O$, Kishida Kagaku KK.) (400 mg) at room temperature for 15 min. The solution was then concentrated under diminished pressure and poured onto water. From the carbon tetrachloride extract, **2** (140 mg, 65%) was isolated.

*Pyrolytic Formation of the Carbonylated Product, Ketone (**5**) from the Complex **4**.* The complex **4** (2.57 g) was heated without solvent very carefully to 110 °C in a flask (100 cc) equipped with a condenser. The decomposition started at 116 °C so violently that some powdery amorphous product blew up through the condenser to the top. The *n*-hexane-soluble part (400 mg) was chromatographically purified. Beside a small amount of the recovered **1**, the yellow crystals of the ketone (**5**) (60 mg) were obtained. Found: C, 27.08; Cl, 67.35%. Calcd for C_7Cl_6O: C, 26.84; Cl, 68.05%. UV: $\lambda_{\max}^{n\text{-hexane}}$ 228 (3.81), 259 (4.55), 267 (4.56), 302 (4.00), 315 (4.24), 330 (4.35) and 348 (4.42); nm (log ε). IR: $\nu_{\max}^{\text{Nujol}}$ 1770 (CO), 1560 and 1495 (C=C) (cm^{-1}).

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