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Synthesis, Spectra, and Crystal Structure of Novel Isomerized Products of (Cyclooctatetraene)dicarbonyl(ethoxyarylcarbene)iron and (8,8-Dihydro-3–5-η-cyclooctatrienyl)tricarbonylaryliron Complexes

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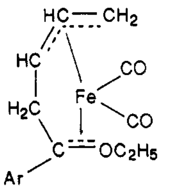
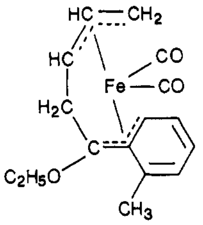
(Cyclooctatetraene)tricarbonyliron(I) reacts with ArLi (Ar = C_6H_5, *p*-, *o*-, or *m*-$CH_3C_6H_4$, *p*-$CF_3C_6H_4$, C_6Cl_5) in ether at −100 °C to yield acylmetalate complexes, from which, by subsequent alkylation with Et_3OBF_4 in CH_2Cl_2 at low temperature or in aqueous solution at 0 °C, orange-red crystalline complexes of composition $C_8H_8(CO)_2FeC(OC_2H_5)Ar$ (IIIa–d) and/or yellow crystalline complexes with composition $C_8H_9(CO)_3FeAr$ (IVa–f) were obtained. It was established that complexes IIIa–d were isomerized products of (cyclooctatetraene)dicarbonyl(ethoxyarylcarbene)iron complexes with two types of structure and complexes IVa–f were (8,8-dihydro-3–5-η-cyclooctatrienyl)tricarbonylaryliron complexes based on elemental analyses and IR, ^1H NMR, and mass spectra as well as single-crystal X-ray structure determinations. A possible reaction mechanism is tentatively proposed and discussed in this paper.

Introduction

Recently, we reported the reaction of (η^4-butadiene)tricarbonyliron with nucleophiles, aryllithium, followed by the alkylation with Et_3OBF_4, from which two new complexes, A and B, were obtained as isomerized (butadiene)dicarbonyl(ethoxyarylcarbene)iron complexes.[2] It would be of interest to see what are the results of the reaction of cyclic polyolefin metal carbonyl compounds with nucleophiles. To further study such an effect of a cyclic polyolefin ligand on the chemistry of a carbene ligand and the reactivity of cycloolefin ligands, we have carried out the reactions of (cyclooctatetraene)tricarbonyliron(I) with aryllithiums followed by alkylation with Et_3OBF_4. A series of novel isomerized products of (cyclooctatetraene)dicarbonyl(ethoxyarylcarbene)iron complexes and (8,8-dihydro-3–5-η-cyclooctatrienyl)tricarbonylaryliron complexes were obtained.



A



B

We now report the syntheses, spectral studies, and X-ray crystal structure determinations of these novel compounds. We have also tentatively proposed and discussed the possible reaction mechanism in this paper.

Results and Discussion

Preparation of Complexes. By analogy to the preparation of general alkoxycarbene complexes[3,4] and isomerized (butadiene)dicarbonyl(ethoxyarylcarbene)iron complexes,[2] equimolar quantities of I and an aryllithium, ArLi (II, Ar = C_6H_5, *p*-, *o*-, or *m*-$CH_3C_6H_4$, *p*-$CF_3C_6H_4$, C_6Cl_5), were used for the reaction in diethyl ether at −100 °C, and the acylmetalate compounds produced were alkylated with Et_3OBF_4 in CH_2Cl_2 at low temperature or in water at 0 °C. The resulting mixture was chromatographed on an alumina column at low temperature, and the crude products were recrystallized from pentane at −80 °C to give orange-red,

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(1) (a) Shanghai Institute of Organic Chemistry. (b) Beijing University.

(2) Chen, J.; Lei, G.; Xu, W.; Jin, X.; Shao, M.; Tang, Y. *J. Organomet. Chem.* **1985**, *286*, 55.

(3) Fischer, E. O.; Beck, H. J.; Kreiter, C. G.; Lanch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162.

(4) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

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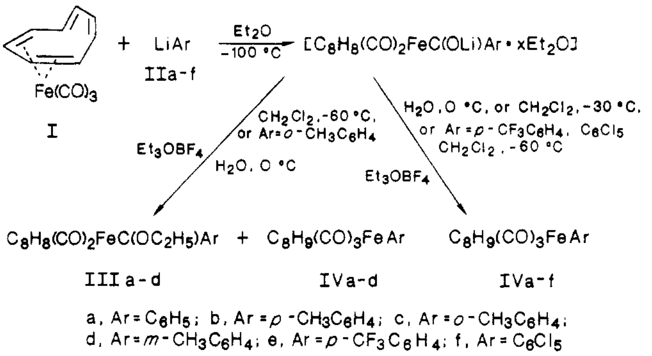
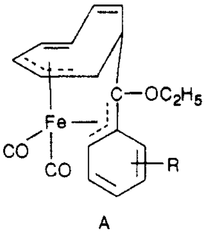
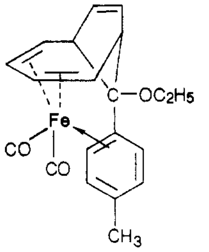
crystalline compounds IIIa–d with general composition $C_8H_8(CO)_2FeC(OC_2H_5)Ar$ and/or yellow, crystalline compounds IVa–d of general composition $C_8H_9(CO)_3FeAr$. However, when an alkyllithium or (diethylamino)lithium is used instead of ArLi, analogous products were not obtained under the same conditions.



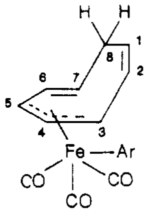
Complexes IIIa–d and IVa–f are diamagnetic and readily soluble in both polar and nonpolar organic solvents. They are highly sensitive to air in solution but stable for a short period in the solid state in air. Although IIIa–d and IVa–f are rather sensitive to temperature, the stability of IVa–f is surprising. In contrast to those analogues of IV reported by Semmelhack et al.,[5] which are transient intermediates on the way to demetalated products, IVa–f are moderately stable at room temperature. This may be due to the protective effect of the aryl group bonded to the Fe atom resulting in an increase of the thermal stability. However, the intermediates $C_8H_8(CO)_2FeC(OLi)Ar{\cdot}xEt_2O$, which are extremely sensitive to air and moisture, decomposed even at −30 °C. On the basis of elemental analyses, spectral analyses, and single-crystal X-ray structure determinations, IIIa–d are formulated as isomerized (cyclooctatetraene)dicarbonyl(ethoxyarylcarbene)iron complexes with two types of structures, A and B, among which IIIa, IIIc, and IIId exist in the form of structure A while IIIb has the form of structure B, and IVa–f are formulated as (8,8-dihydro-3–5-η-cyclooctatrienyl)tricarbonylaryliron complexes.



A
IIIa, R=H
c, R=o-CH3
d, R=m-CH3



B
IIIb



IVa-f

Similar to the reaction of (η^4-butadiene)tricarbonyliron with aryllithiums, the reaction between I and aryllithium reagents and subsequent alkylation with Et_3OBF_4 yields novel isomerized (cyclooctatetraene)dicarbonyl(ethoxyarylcarbene)iron complexes (IIIa–d) and/or (8,8-dihydro-3–5-η-cyclooctatrienyl)tricarbonylaryliron complexes (IVa–f), instead of the normal olefin-ligated carbene complexes. It is found that the formation of the various isomerized products depends not only on alkylation temperature but also on the nature of substituents of the aryl nucleophiles.

(1) The Influence of Alkylation Temperature. When the (acylcarbonyl)lithium compounds produced by reaction of nucleophiles IIa–d with I were alkylated with Et_3OBF_4 in CH_2Cl_2 at −60 °C, the resulting products IIIa–d were accompanied by small amounts of IVa–d. However, alkylation in CH_2Cl_2 at −30 °C or in water at 0 °C gave only IVa–d. The (acylcarbonyl)lithium compound formed by reaction of II_c with I was an exception; it was alkylated with Et_3OBF_4 in CH_2Cl_2 at either −60 or −30 °C or in water at 0 °C to give the same mixture of IIIc and IVc. These facts indicated that the resulting products formed depend on the alkylation temperature but not on the solvents.

(2) The Influence of the Nature of Substituents of Nucleophiles. When IIa–d, in which the aryl substituent is a phenyl or a tolyl group, were used as nucleophilic reagents for reaction with I, the acylmetalate intermediates formed were alkylated with Et_3OBF_4 in CH_2Cl_2 at −60 °C to give isomerized title complexes IIIa–d accompanied by IVa–d. However, when IIe and IIf, in which the aryl substituent is an electron-withdrawing group, were used in the reaction, alkylation of the acylmetalate intermediates in CH_2Cl_2 at −60 °C or in aqueous solution at 0 °C gave only (8,8-dihydro-3–5-η-cyclooctatrienyl)tricarbonylaryliron complexes IVe and IVf. This indicates that the electronic effect of the substituents of nucleophiles plays a significant role in determining the resulting products.

About the reaction mechanism, we speculate that the normal (acylcarbonyl)lithium compounds A or B were formed when I reacted with aryllithium. Indeed, we observed the formation of acylmetalate compounds as yellow precipitates and succeeded in separating the crystalline compound $C_8H_8(CO)_2FeC(OLi)C_6H_5{\cdot}xEt_2O$ (ν_{CO} 1955, 1802 cm^{-1} (CH_2Cl_2)) from the reaction mixtures. That the acylmetalate intermediates formed by reaction of I with IIa–d on alkylation with Et_3OBF_4 in CH_2Cl_2 at −60 °C gave IIIa–d accompanied by IVa–d while in water at 0 °C only IVa–d were obtained suggests a possible rationale: an equilibrium mixture of A and B which, depending on the reaction conditions, alkylation (route a) or protonation (route b), yields mainly complexes III or IV, as shown in Scheme I.

The alkylation of the acylmetalate intermediate formed by reaction of I with IIe or IIf, even at −60 °C, proceeded according to route b to give IVe or IVf due to the extreme lability of its intermediate compound, caused by the strong electron-withdrawing effect of p-$CF_3C_6H_4$ and C_6Cl_5 groups. The mechanism postulated above is rather similar to that of nucleophilic addition to cyclodiene metal complexes reported by Semmelhack et al.[5]

The reactivities of these new complexes are under investigation.

Spectral Studies

Infrared Spectra. The IR spectral data of complexes IIIa–d and IVa–f are given in Table I. IIIa–d and IVa–f show the two and three strong CO absorption bands in the ν(CO) region which is consistent with the presence of carbonylmetal compounds with general formulas $(CO)_2MLL'$ and $(CO)_3MLL'$, respectively.

The data given in Table I showed that the different aryl substituents exert no notable influence on the ν(CO) frequency in complexes IIIa–d but exert a little influence on the ν(CO) frequency in complexes IVa–f.

^1H NMR Spectra. The ^1H NMR spectral data of IIIa–d and IVa–f in acetone-d_6 at 20 °C are given in Tables II and III, respectively. All of these complexes showed complex proton signals attributed to the cycloolefin ligand, arising from a σ–π rearrangement of the cyclooctatetraene ligand. As a result of rearrangement, the structure of the

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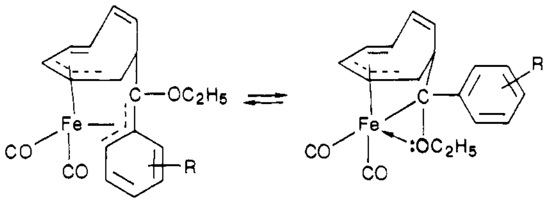
[5] (a) Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379. (b) Semmlhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497. (c) Semmelhack, M. F.; Herndon, J. W. *J. Organomet. Chem.* **1984**, *265*, C15.

Table I. IR Spectra of IIIa-d and IVa-f in the ν(CO) Region

complex	ν(CO), cm^{-1} CH_2Cl_2	 pentane
IIIa	1980 vs, 1920 vs	1988 vs, 1983 sh, 1935 vs, 1928 sh
IIIb	1975 vs, 1910 vs	1998 vs, 1942 vs
IIIc	1980 vs, 1920 vs	1990 vs, 1980 sh, 1960 sh, 1940 vs
IIId	1981 vs, 1918 vs	1996 vs, 1975 sh, 1942 vs, 1920 sh
IVa	2048 vs, 1993 sh, 1979 vs	2050 vs, 2000 vs, 1995 vs
IVb	2055 vs, 2000 vs, 1993 vs	2058 vs, 2002 vs, 1995 vs
IVc	2040 vs, 2005 vs, 1948 vs	2050 vs, 2005 vs, 1990 vs
IVd	2051 vs, 1998 sh, 1986 vs	2058 vs, 2001 vs, 1992 vs
IVe	2057 vs, 2006 vs, 1984 vs	2060 vs, 2008 vs, 2000 vs
IVf	2060 vs, 2015 vs, 1960 vs	2045 vs, 2005 vs, 1990 vs

cycloolefin ligand consists of (1) a π-allyl and one carbon atom of cycloolefin ring bonding to the "carbene" carbon in IIIa, IIIc, and IIId, (2) a η^4-bond and two carbon atoms of cycloolefin ring bonding to "carbene" carbon in IIIb, or (3) a π-allyl and the addition of a hydrogen abstracted from solvent to the C-8 ring position in IVa-f. Thus, the proton signals of the original cycloolefin ligand shifted accordingly.

Interestingly, the ^{1}H NMR spectra of IIIa and IIId showed two different proton signals attributed to $-OCH_2CH_3$ group, in addition to the expected proton signals. This suggested that in solution there existed, as in $(CO)_5CrC(OCH_3)C_6H_5$[4] and $C_4H_6(CO)_2FeC(OC_2H_5)Ar$,[2] two probable cis-trans geometrical isomers (with regard to the C(17)-O(3) bond), arising from the difference in steric arrangement of the ethyl and aryl groups, since C(17)-O(3) (1.397 (6) Å) is a partial double bond on the basis of the single-crystal X-ray structure analyses of IIIa. It is not excluded that a possible alternative explanation is the presence of two differently coordinated species, in equilibrium with one another, in solution. However, in the case of IIIc, in which C(5)-O(3) (1.395 Å) is also a partial double bond, no analogous cis isomer has been isolated, perhaps due to the steric hindrance of the methyl group at the *o*-tolyl substituent.



Mass Spectra. The mass spectral data of IIIa-d and IVa-f given in Tables IV and V, respectively, provided a series of characteristic ions bearing useful structure information. All of the complexes showed, besides their molecular ions, the principal fragments produced by successive loss of CO ligand and feature ion peaks from fragmentation generated by further cleavage of these principal fragments.

Description and Discussion of Structure of the Various Complex Molecules

On the basis of the results of the structure analyses, the molecular configurations of IIIa-c, IVa, and IVe are shown in Figures 1-5, respectively. Structure analyses demonstrate that the bonding mode for the central atom and ligands in all these molecular structures is governed by the "18-electron rule". The various expressions of the rule in

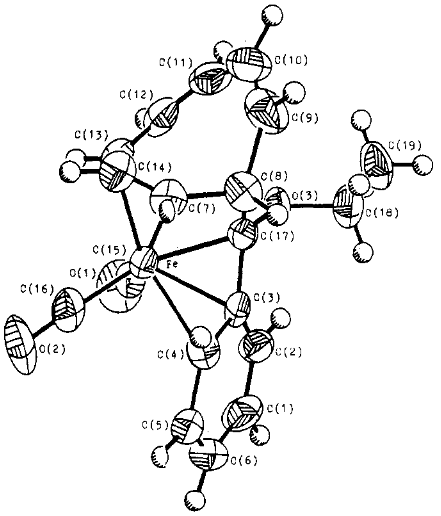


Figure 1. Molecular structure for IIIa.

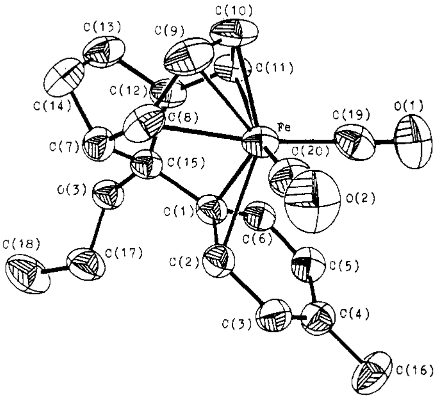


Figure 2. Molecular structure for IIIb.

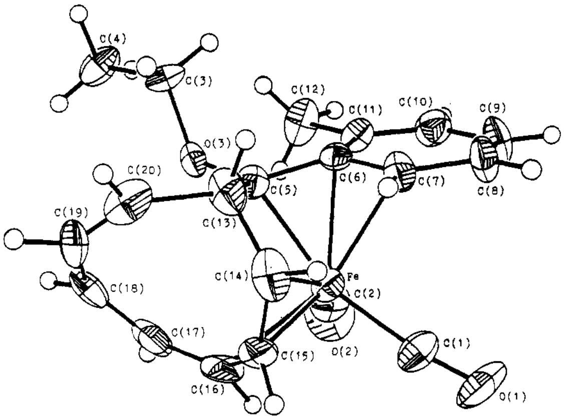


Figure 3. Molecular structure for IIIc.

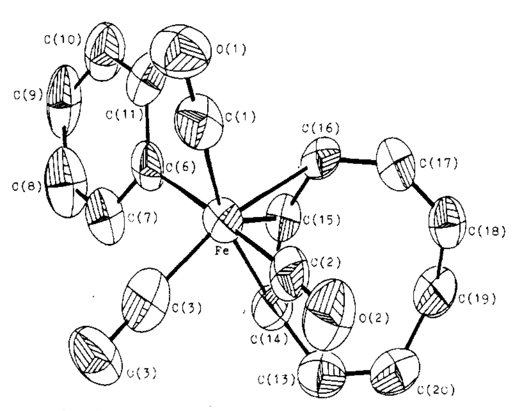


Figure 4. Molecular configuration of IVa.

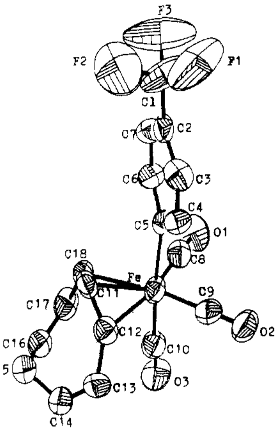
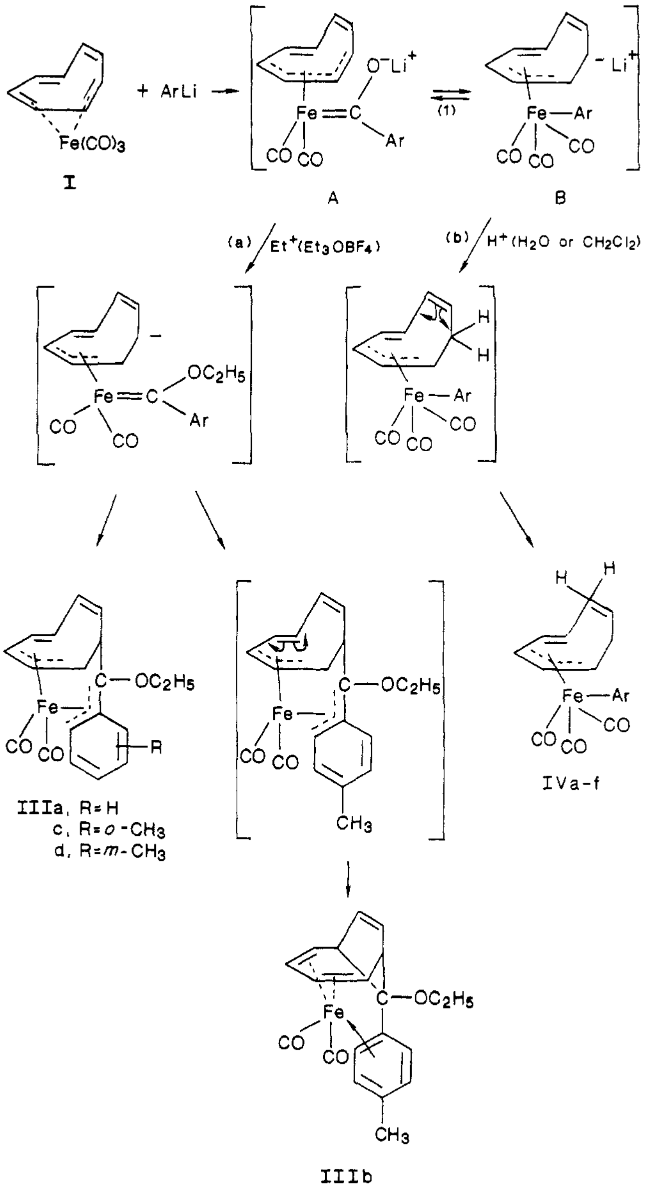


Figure 5. Molecular configuration of IVe.

Scheme I

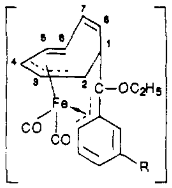
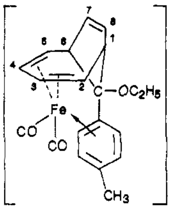
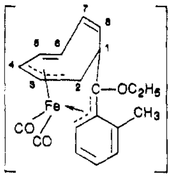


these structures are very interesting.

In the dicarbonyliron complexes IIIa and IIIc, the bonding mode is analogous to that of isomerized (butadiene)(carbene)iron complexes:[2] (i) This bonding mode may be understood as the breaking of one of the double bonds of cyclooctatetraene and forming a new bond with the "carbene carbon" in the "carbene structure", resulting in the formation of isomerized title complexes. For convenience, the carbon atom that is bonded to the ethoxy group is taken as the "carbene carbon" in this paper. (ii) Among the 18 electrons in the valence shell of the central atom, besides the eight electrons that belong to Fe(0) and two pairs of electrons provided by the two carbonyl carbons, the other six electrons were provided by the bonding orbitals of two allyl-like $\pi_3{}^3$-bondings composed of two carbon atoms (C(3), C(4) in IIIa and C(6), C(7) in IIIc) of the benzene ring, three p_z orbitals of the adjacent "carbene" carbon atom (C(17) in IIIa and C(5) in IIIc), and the corresponding three π-electrons (the $\pi_3{}^3$ is defined as the nonlocalized π-bonding involving three electrons and the p_z orbital of three atoms).

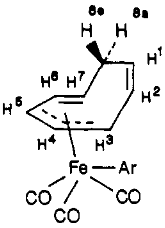
Two very interesting aspects are mentioned here in passing: (i) In order to participate in $\pi_3{}^3$-bonding with the

Table II. ^1H **NMR Spectra of Complexes IIIa–d in Acetone-d_6 at 20 °C**[a]

	assign	chem shift (δ)	rel intens	mult
 IIIa, R=H	$-OCH_2CH_3$	0.78 (cis)	3	t
		1.25 (trans)		t
	1	2.96	1	m
	$-OCH_2CH_3$	3.42 (cis)	2	q
		3.74 (trans)		q
	2	3.82	1	m
	4	4.20	1	t
	3	4.79	1	t
	5–8	5.50	2	m
		5.78	2	m
	$-C_6H_5$	7.25	2	m
		7.48	1	m
		7.70	1	m
		7.88	1	m
IIId, R = CH_3	$-OCH_2CH_3$	0.88 (cis)	3	t
		1.24 (trans)		t
	$-C_6H_4CH_3$	2.41	3	s
	1	3.02	1	m
	$-OCH_2CH_3$	3.49 (cis)	2	q
		3.72 (trans)		q
	2	3.76	1	m
	4	4.24	1	m
	3	4.78	1	m
	5–8	5.28–5.70	4	m
	$-CH_3C_6H_4$	6.97	1	m
		7.20	1	m
		7.40	1	m
		7.60	1	m
 IIIb	$-OCH_2CH_3$	1.23	3	t
	$-C_6H_4CH_3$	2.23	3	s
	1,6	2.96	2	m
	$-OCH_2CH_3$	3.46	2	q
	2,5	3.78	2	m
	7	4.12	1	t
	8	4.70	1	t
	4	5.46	1	m
	3	5.68	1	m
	$-CH_3C_6H_4$	7.18	2	m
		7.60	1	m
		7.80	1	m
 IIIc	$-OCH_2CH_3$	1.14	3	t
	$-CH_3C_6H_4$	2.70	3	s
	1	2.84	1	m
	$-OCH_2CH_3$	3.46	2	q
	2	3.90	1	t
	4	4.30	1	t
	3	4.66	1	t
	5–8	5.56	2	m
		5.75	2	m
	$-CH_3C_6H_4$	7.02	1	m
		7.10	1	m
		7.25	2	m

[a] TMS as internal reference.

Table III. ^{1}H NMR Spectra of Complexes IVa–f in Acetone-d_6 at 20 °C[a]



complex	δ(cycloolefin proton)[a] H^{1,7}	H^{2,6}	H^{3,5}	H^4	H^{8a}	H^{8e}	δ(aryl proton)	δ(CH$_3$)
IVa	5.80 (m, 2)	6.36 (m, 2)	5.55 (m, 2)	5.15 (b, 1)[b]	2.88 (b, 1)	2.85 (b, 1)	7.40 (m, 2) 7.05 (m, 3)	
IVb	5.78 (m, 2)	6.32 (m, 2)	5.60 (m, 2)	5.12 (b, 1)	2.89 (m, 1)	2.86 (m, 1)	7.38 (m, 2) 7.02 (m, 2)	2.24 (s, 3)
IVc	5.60 (m, 2)	6.34 (m, 2)	5.44 (m, 2)	5.08 (b, 1)	2.89 (m, 1)	2.86 (m, 1)	7.20 (m, 2) 7.14 (m, 2)	2.14 (s, 3)
IVd	5.76 (m, 2)	6.35 (m, 2)	5.56 (m, 2)	5.12 (b, 1)	3.02 (m, 1)	2.91 (m, 1)	7.23 (m, 2) 6.96 (m, 2)	2.25 (s, 3)
IVe	5.65 (m, 2)	6.44 (m, 2)	5.25 (m, 2)	3.32 (t, 1)	2.90 (m, 1)	2.68 (m, 1)	7.66 (m, 2) 7.30 (m, 2)	
IVf	5.90 (m, 2)	6.16 (m, 2)	5.64 (m, 2)	5.18 (m, 1)	2.96 (m, 1)	2.94 (m, 1)		

[a] TMS as internal reference. The number of the H proton in cycloolefin ligand for IVa–f. [b] b = broad.

Table IV. Characteristic Peaks (m/e) of Mass Spectra for IIIa–d[a]

ion	IIIa	IIIb	IIIc	IIId
M$^+$	350	364	364	364
M - CO$^+$	322	336	336	336
M - 2CO$^+$	294	308	308	308
M - 2 CO - C$_2$H$_5$$^+$	265	279	279	279
M - 2CO - C$_2$H$_5$OH$^+$	248	262	262	262
M - 2CO - COC$_2$H$_5$$^+$	237	251	251	251
M - 2CO - C$_8$H$_8$$^+$	190	204	204	204
M - Fe(CO)$_2$$^+$	238	252	252	252
COC$_2$H$_5$Ar$^+$	134	148	148	148
FeAr$^+$	133	147	147	147
ArCO$^+$	105	119	119	119
C$_8$H$_8$$^+$	104	104	104	104
Ar$^+$	77	91	91	91
Fe	56	56	56	56

[a] M = molecular ion.

Table V. Characteristic Peaks (m/e) of Mass Spectra for IVa–IVf[a]

ion	IVa	IVb	IVc	IVd	IVe	IVf
M$^+$	322	336	336	336	390	492
M - CO$^+$	294	308	308	308	362	464
M - 2CO$^+$	266	280	280	280	334	436
M - 3CO$^+$	238	252	252	252	306	408
M - 3CO - H$^+$	237	251	251	251	305	407
M - 3CO - 2H$^+$	236	250	250	250	304	406
C$_8$H$_9$Fe(CO)$_2$ - H$^+$	216	216	216	216	216	216
C$_8$H$_9$Fe(CO) - H$^+$	188	188	188	188	188	188
C$_8$H$_9$Fe - H$^+$	160	160	160	160	160	160
FeAr$^+$	133	147	147	147	201	303
C$_8$H$_9$$^+$	105	105	105	105	105	105
Ar$^+$	77	91	91	91	145	248
Fe$^+$	56	56	56	56	56	56

[a] M = molecular ion.

Fe atom, the benzene ring has resumed the Kekulé structural character to a certain extent, which is demonstrated by the alternate change of bond lengths in the benzene ring. (ii) The "carbene" carbon atom in IIIa and IIIc has become four-coordinate, but its configuration has not become tetradral. That the sum of the bond angles around the "carbene" carbon is very close to 360° means that the "carbene" carbon atom forms three σ-bonds with three adjacent atoms by using its sp^2-hybridized orbitals. Correspondingly, each of the three atoms should contribute one p$_z$ orbital to form the π_3^3 fragment to interact further with the orbital of the Fe atom. From the stereo figures of the molecular configuration it can be seen that the normal of the plane of the three atoms, viz., the z direction of the p$_z$ orbital is almost parallel to the perpendicular from the Fe atom to the plane of the three atoms. This strongly shows that such allyl-like π_3^3-bonding to the Fe atom is in a "side-on mode".

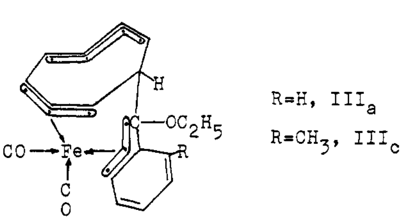


Figure 6. The bonding mode in IIIa and IIIc.

In the eight-membered rings of structures IIIa and IIIc, all except one carbon atom (C(8) in IIIa and C(13) in IIIc) are transformed into C(sp^3)-type atoms arising from its bonds to a "carbene" carbon atom. All of the other atoms are C(sp^2)-type atoms, keeping one π-electron. Three of them and their three π-electrons constitute another allyl-like π_3^3-bonding unit to combine with the Fe atom. The bonding mode in this kind of structure can be expressed by Figure 6. However, there is a difference between molecules IIIa and IIIc owing to the steric hindrance caused by the ortho methyl group of the benzene ring. This difference was obvious in the ^{1}H NMR spectra as mentioned above.

In IIIb, we have verified a very interesting structure that has not been previously reported. The "carbene" carbon is no longer ligated with the Fe atom but bonded to C(7) and C(12) in the middle of the eight-membered ring in a cross-on mode that led to the transformation of C(7) and C(12) into C(sp^3)-type atoms and separated the π-bonding system of the eight-membered ring into two parts of π_2^2 and π_4^4, corresponding to C(13)–C(14) and C(8)–C(9)–C(10)–C(11), respectively. The π_4^4-bonding orbital interacts with the Fe atom. In order to satisfy the 18-electron rule, only the localized π-bonding of two carbon atoms of the phenyl group interact with the Fe atom. This phenyl group also obviously exhibits Kekulé character. From the stereo molecular structure figure we find that the eight-

Table VI. Crystallographic Data for the Five Complexes IIIa–c, IVa, and IVe

	IIIa	IIIb	IIIc	IVa	IVe
mol formula	$C_{19}H_{18}O_3Fe$	$C_{20}H_{20}O_3Fe$	$C_{20}H_{20}O_3Fe$	$C_{17}H_{14}O_3Fe$	$C_{18}H_{13}O_3F_3Fe$
cryst system	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	C_{2h}^5—$P2_1/n$	C_i^1—$P\bar{1}$	C_{2v}^5—$Pbc2_1$	C_{2h}^5—$P2_1/c$	C_{2h}^5—$P2_1/c$
cell dimens					
a, Å	10.427 (7)	8.232 (3)	10.428 (4)	7.348 (5)	10.611 (2)
b, Å	14.020 (7)	8.311 (3)	11.580 (3)	7.891 (2)	12.023 (5)
c, Å	12.022 (4)	12.857 (4)	14.126 (3)	26.248 (10)	14.118 (4)
α, deg		82.642 (27)			
β, deg	109.624 (39)	87.866 (26)		91.82 (5)	109.28 (2)
γ, deg		75.094 (25)			
V, Å^3	1655.3	844.0	1705.8	1521.3	1700.1
Z	4	2	4	4	4
D_{calcd}, g/cm^3	1.41	1.43	1.42	1.41	1.52
μ(Mo Kα), cm^{-1}	9.5	9.3	9.3	10.3	9.6
F(000)	728	380	712	664	792
radiatn λ(Mo Kα), Å	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
monochromator	graphite crystal	graphite crystal	graphite crystal	graphite crystal	graphite crystal
data collectn mode	θ–2θ	θ–2θ	ω	ω	θ–2θ
scan speed, deg/min	variable 4–29.3	variable 4–29.3	variable 4–29.3	variable 7–29.3	variable 4–29.3
angle range, deg	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 50$	$0 \le 2\theta \le 50$	$0 \le 2\theta \le 50$	$3 \le 2\theta \le 45$
total unique data	1962	3217	1156	2110	2507
obsd data $F > 3\sigma(F)$	1534	2495	954	1311	1856
R	0.0523	0.0474	0.084	0.082	0.0581
R_w	0.0432	0.0417	0.0635	0.0644	0.0515
w			$1/[\sigma^2(F) + 0.0005F^2]$	$1/[\sigma^2(F) + 0.0002F^2]$	$1/[\sigma^2(F) + 0.0002F^2]$

membered ring exhibits a particularly apparent boat conformation.

In the tricarbonyl complexes IVa and IVe, the 18 electrons participating in the central atom valence configuration consist of the eight electrons of the Fe atom, three pairs of electrons provided by the carbonyl carbons, and the other four electrons, one of which is a σ-electron provided by the phenyl group ligating the Fe atom in an end-on mode and three of which are the π-electrons provided by an allyl-type π_3^3-bonding orbital composed of three p_z orbitals of the carbon atoms and three π-electrons of the cyclooctatetraene ligand, bonded side on to the Fe atom.

There are three different kinds of bonding of the cyclooctatetraene rings in the five crystal structures determined in this paper. In IIIa and IIIc, the eight-membered ring has one C(sp^3)-type atom connecting to the "carbene" carbon using σ-bonding and the other three atoms connecting to the Fe atom using π_3^3-bonding in the side-on mode. In IIIb, two C(sp^3) atoms of eight-membered ring are bonded to the "carbene" carbon using σ-bonding and the other four C(sp^2) atoms are bonded to the Fe atom using π_4^4-bonding in the side-on mode. In the case of IVa and IVe, the cyclooctatetraene ligand does not participate in any σ-bonding beyond the ring and only provides their allyl-type π_3^3-bonding for bonding side on to the Fe atom. The great variety of the bonding modes of cyclooctatetraene in these organometallic compounds is quite interesting.

Experimental Section

Preparation of Complexes. IR, ^{1}H NMR, and mass spectra were recorded on Perkin-Elmer 638, Varian XL-200, and Finnigan 4021 GC/MS/DS spectrometers, respectively.

All operation must be carried out under a N_2 atmosphere. All solvents employed were dried over Na, CaH_2, and P_2O_5 and saturated with N_2. The alumina (neutral) used for chromatography was deoxygenated in high vacuum, deactivated with 5% w/w water, and stored under N_2. I and aryllithium reagents used were prepared as described in ref 6 and ref 7 and 9–12, respectively.

Table VII. Atom Coordinates (×10^4) and Temperature Factors (×10^3) of IIIa

atom	x	y	z	U_{eq}, Å^2
Fe	1086 (1)	2276 (1)	3970 (1)	39 (3)
C(1)	931 (8)	4663 (4)	2331 (9)	67 (3)
C(2)	58 (7)	4240 (4)	2791 (6)	52 (3)
C(3)	4472 (5)	8756 (4)	1091 (5)	40 (2)
C(4)	3030 (5)	8747 (4)	504 (5)	44 (2)
C(5)	2864 (7)	4171 (4)	3975 (7)	55 (3)
C(6)	2361 (7)	4618 (5)	2940 (7)	67 (4)
C(7)	3834 (5)	7193 (5)	−785 (5)	50 (2)
C(8)	24 (6)	2924 (4)	5609 (5)	50 (2)
C(9)	−1097 (7)	2529 (5)	6010 (6)	72 (3)
C(10)	−2059 (7)	1893 (5)	5478 (7)	77 (4)
C(11)	−2362 (7)	1465 (5)	4320 (7)	74 (4)
C(12)	−1520 (7)	1149 (4)	3795 (6)	67 (3)
C(13)	5023 (6)	6056 (4)	820 (6)	58 (3)
C(14)	4006 (6)	6331 (5)	−250 (6)	59 (3)
C(15)	417 (6)	2127 (4)	2425 (5)	53 (3)
C(16)	2732 (6)	1865 (4)	4035 (5)	51 (3)
C(17)	5368 (5)	8191 (4)	692 (4)	36 (2)
C(18)	−2327 (5)	4107 (4)	4048 (6)	58 (3)
C(19)	−3834 (5)	4075 (5)	3504 (6)	75 (3)
O(1)	−38 (5)	1964 (3)	1421 (4)	87 (2)
O(2)	3820 (4)	1643 (3)	4099 (4)	87 (2)
O(3)	−1751 (4)	3296 (2)	3661 (3)	43 (2)

1. $C_8H_8(CO)_2FeC(OLi)C_6H_5\cdot xEt_2O$. To a solution of 1.5 g (6.1 mmol) of I in 100 mL of ether at −100 °C was added dropwise 6.1 mmol of LiC_6H_5[7] in 20 mL of ether. The mixture was slowly warmed to −70 °C and an orange precipitate separated from the reaction mixture. After stirred at −70 °C for 3 h, the dark red solution was decanted. The residual orange crystalline product was washed with ether at −60 °C and dried in high vacuum at −60 °C; yield 1.85 g.

2. Alkylation of $C_8H_8(CO)_2FeC(OLi)C_6H_5\cdot xEt_2O$ in CH_2Cl_2 at −60 °C. $C_8H_8(CO)_2FeC(OC_2H_5)C_6H_5$ (IIIa) and $C_8H_9(CO)_3FeC_6H_5$ (IVa). $C_8H_8(CO)_2FeC(OLi)C_6H_5\cdot xEt_2O$ (0.54 g) was dissolved in 30 mL of CH_2Cl_2 at −60 °C. To this solution was added dropwise 0.40 g of Et_3OBF_4[8] in 20 mL of CH_2Cl_2 with stirring within 20 min. The reaction mixture turned from dark

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Table VIII. Atom Coordinates (×10⁴) and Temperature Factors (×10³) for IIIb and IIIc

	IIIb				IIIc			
atom	*x*	*y*	*z*	U_{eq}, Å^2	*x*	*y*	*z*	U_{eq}, Å^2
Fe	2906 (1)	8525 (1)	3145 (1)	37 (2)	8591 (1)	1534 (1)	5000 (0)	33 (1)
C(1)	−413 (4)	633 (4)	7649 (3)	33 (1)	203 (10)	1493 (10)	5481 (8)	44 (4)
C(2)	−34 (4)	618 (4)	6578 (2)	37 (1)	8499 (9)	−1 (8)	5603 (13)	45 (3)
C(3)	711 (4)	1840 (5)	6030 (3)	42 (1)	5221 (9)	1890 (10)	3114 (8)	37 (4)
C(4)	1060 (4)	3073 (4)	6512 (3)	44 (1)	3934 (10)	1295 (12)	3053 (10)	62 (5)
C(5)	677 (4)	3099 (4)	7590 (3)	42 (1)	7074 (9)	1965 (8)	4086 (7)	27 (3)
C(6)	−24 (4)	1941 (4)	8129 (2)	37 (1)	8176 (8)	1586 (9)	3516 (7)	29 (3)
C(7)	−1499 (4)	−2063 (4)	7805 (3)	44 (1)	9296 (9)	2313 (11)	3625 (8)	43 (4)
C(8)	−2785 (5)	−1126 (5)	6974 (3)	45 (1)	474 (10)	1904 (11)	3187 (9)	49 (4)
C(9)	−4414 (5)	−146 (6)	7138 (3)	55 (2)	577 (11)	919 (10)	2754 (9)	52 (5)
C(10)	−4764 (4)	993 (5)	7874 (3)	51 (2)	9439 (10)	219 (11)	2645 (8)	46 (4)
C(11)	−3498 (4)	1148 (5)	8539 (3)	39 (1)	8291 (9)	519 (8)	3016 (7)	29 (3)
C(12)	−2181 (4)	−262 (5)	9124 (3)	40 (1)	7177 (10)	−287 (9)	2868 (10)	50 (4)
C(13)	−2756 (5)	−1828 (5)	9440 (3)	54 (2)	6989 (10)	3230 (8)	4448 (9)	43 (4)
C(14)	−2351 (5)	−2845 (5)	8729 (3)	55 (2)	7969 (10)	3295 (8)	5215 (9)	41 (5)
C(15)	−758 (4)	−852 (4)	8349 (3)	35 (1)	7989 (11)	2733 (15)	6027 (9)	67 (6)
C(16)	1872 (5)	4359 (6)	5935 (3)	68 (2)	7326 (11)	1634 (10)	6244 (7)	41 (4)
C(17)	−2192 (5)	12353 (6)	1624 (4)	60 (2)	6014 (15)	1225 (14)	6085 (10)	48 (5)
C(18)	−3269 (6)	13814 (6)	1009 (4)	77 (2)	4970 (11)	1834 (9)	5748 (7)	37 (4)
C(19)	3321 (4)	6337 (5)	3155 (3)	48 (2)	4880 (11)	2995 (11)	5385 (8)	57 (5)
C(20)	3187 (4)	8225 (5)	4525 (3)	47 (1)	5692 (10)	3606 (9)	4870 (11)	47 (4)
O(1)	3613 (4)	4908 (4)	3176 (2)	79 (1)	1273 (8)	1443 (8)	5669 (7)	72 (4)
O(2)	3425 (4)	8008 (4)	5412 (2)	77 (1)	8427 (8)	−984 (7)	5111 (12)	74 (4)
O(3)	696 (3)	−1749 (3)	8954 (2)	44 (1)	5915 (8)	1398 (7)	3923 (6)	30 (3)

Table IX. Atom Coordinates (×10⁴) and Thermal Parameters (×10³) of IVa and IVe

	IVa				IVe			
atom	*x*	*y*	*z*	U_{eq}, Å^2	*x*	*y*	*z*	U_{eq}, Å^2
Fe	1670 (2)	2220 (2)	1260 (1)	45 (1)	1055 (1)	2172 (1)	3373 (1)	45 (1)
O(1)	3887 (11)	3075 (12)	2174 (3)	90 (4)	−432 (5)	1620 (4)	1281 (3)	90 (2)
O(2)	2462 (12)	5675 (10)	884 (3)	74 (4)	1901 (4)	4427 (4)	3061 (4)	93 (2)
O(3)	−1897 (10)	3361 (9)	1577 (3)	78 (3)	3493 (4)	1244 (4)	3094 (3)	87 (2)
C(1)	3017 (16)	2687 (15)	1820 (4)	67 (5)	−4274 (7)	4243 (6)	3731 (6)	97 (4)
C(2)	2130 (16)	4318 (15)	1003 (4)	50 (4)	−3074 (5)	3786 (5)	3560 (4)	53 (2)
C(3)	−488 (14)	2900 (13)	1449 (4)	58 (4)	−1868 (6)	4337 (5)	3954 (4)	56 (3)
C(4)					−724 (5)	3897 (5)	3854 (4)	52 (2)
C(5)					−709 (4)	2903 (5)	3365 (3)	42 (2)
C(6)	1043 (16)	−27 (12)	1632 (3)	49 (4)	−1943 (5)	2394 (4)	2939 (4)	50 (2)
C(7)	2341 (17)	−906 (15)	1915 (4)	69 (5)	−3104 (5)	2808 (5)	3036 (4)	60 (2)
C(8)	1927 (19)	−2426 (15)	2141 (4)	91 (6)	149 (5)	1814 (4)	2102 (4)	58 (2)
C(9)	208 (18)	−3137 (13)	2099 (4)	86 (6)	1583 (5)	3546 (5)	3192 (4)	59 (2)
C(10)	−1042 (17)	−2260 (4)	1814 (4)	81 (5)	2584 (6)	1575 (5)	3252 (4)	60 (3)
C(11)	−676 (16)	−733 (14)	1578 (4)	64 (5)	894 (5)	1521 (4)	4706 (4)	46 (2)
C(12)					2023 (5)	2213 (5)	5016 (4)	53 (2)
C(13)	594 (13)	2677 (12)	105 (3)	47 (4)	3442 (5)	1912 (5)	5353 (4)	62 (3)
C(14)	729 (14)	1342 (12)	495 (4)	44 (4)	3942 (6)	10935 (5)	5690 (5)	72 (3)
C(15)	2247 (16)	451 (12)	695 (4)	42 (4)	3164 (6)	9926 (6)	5762 (5)	73 (3)
C(16)	3970 (15)	1135 (13)	843 (4)	55 (4)	2616 (6)	9341 (5)	4779 (5)	68 (3)
C(17)	5083 (13)	2370 (14)	593 (4)	62 (5)	1556 (6)	9677 (5)	4022 (5)	62 (3)
C(18)	5001 (13)	2788 (14)	104 (4)	60 (4)	671 (5)	617 (4)	4037 (4)	49 (2)
C(19)	3610 (12)	2105 (13)	−278 (4)	59 (4)				
C(20)	1816 (13)	2974 (12)	−244 (3)	51 (4)				
F(1)					−4437 (6)	5238 (4)	3707 (7)	237 (6)
F(2)					−4386 (6)	3921 (6)	4551 (5)	219 (4)
F(3)					−5369 (5)	3825 (7)	3155 (6)	218 (5)

red to orange-red. After being stirred at −60 °C for 0.5 h, the solvent was removed in high vacuum at −50 °C and the residue was chromatographed on alumina at −20 °C with pentane as eluant. The lower red zone which eluted down first was collected; then the upper yellow zone was eluted with pentane/ether (10/1) as eluant. After removal of solvents from the above two eluates under vacuum, the residues were recrystallized from pentane at −80 °C. From the first fraction 0.36 g of orange-red needles of IIIa was obtained; mp 93 °C dec. Anal. Calcd for $C_{19}H_{18}O_3Fe$ (350.20): C, 65.17; H, 5.27; Fe, 15.59; mol wt, 350 (mass spectrum, based on ^{56}Fe). Found: C, 65.31; H, 5.44; Fe, 15.81. From the second fraction 0.08 g of pale yellow needles of IVa was obtained; mp 48–49 °C dec. Anal. Calcd for $C_{17}H_{14}O_3Fe$ (322.15): C, 63.38; H, 4.38; O, 14.90; Fe, 17.34%; mol wt, 322 (mass spectrum). Found: C, 63.52; H, 4.67; O, 15.35; Fe, 17.76.

3. Alkylation of $C_8H_8(CO)_2FeC(OLi)C_6H_5{\cdot}xEt_2O$ in CH_2Cl_2 at −30 °C. $C_8H_9(CO)_3FeC_6H_5$ (IVa). $C_8H_8(CO)_2FeC(OLi)C_6H_5{\cdot}xEt_2O$ (0.5 g) was dissolved in 30 mL of CH_2Cl_2 at −30 °C. Subsequent alkylation in a similar manner as described in (2) gave 0.38 g of pale yellow crystals; mp 48 °C dec. Anal. Calcd for $C_{17}H_{14}O_3Fe$ (322.15): C, 63.38; H, 4.38; Fe, 17.34; mol wt, 322 (mass spectrum). Found: C, 63.77; H, 4.48; Fe, 17.58.

4. Alkylation of $C_8H_8(CO)_2FeC(OLi)C_6H_5{\cdot}xEt_2O$ in H_2O at 0 °C. $C_8H_9(CO)_3FeC_6H_5$ (IVa). $C_8H_8(CO)_2FeC(OLi)C_6H_5{\cdot}xEt_2O$ (0.5 g) was dissolved in 50 mL of N_2-saturated water at 0 °C and covered with pentane. Et_3OBF_4 was subsequently added portionwise with stirring to the aqueous solution until it became acidic. The aqueous solution was extracted with pentane, and the extracts were dried over anhydrous Na_2SO_4. Further treatment in a similar manner as described in (2) gave 0.42 g of pale yellow needles of IVa, mp 48–49 °C dec. Anal. Calcd for $C_{17}H_{14}O_3Fe$ (322.15): C, 63.38; H, 4.38; O, 14.90; Fe, 17.34; mol wt, 322 (mass spectrum). Found: C, 63.25; H, 4.35; O, 15.25; Fe, 17.0.

Table X. Bond Lengths (Å) and Bond Angles (deg) of IIIa

Fe–C(15)	1.764 (6)	C(3)–C(4)	1.430 (7)	C(13)–C(14)	1.418 (8)
Fe–C(16)	1.787 (6)	C(4)–C(5)	1.416 (10)	C(14)–C(7)	1.352 (9)
Fe–C(3)	2.149 (5)	C(5)–C(6)	1.334 (10)	C(15)–O(1)	1.161 (7)
Fe–C(4)	2.260 (5)	C(6)–C(1)	1.425 (9)	C(16)–O(2)	1.154 (8)
Fe–C(7)	2.158 (6)	C(7)–C(8)	1.531 (8)	C(17)–O(3)	1.397 (6)
Fe–C(13)	2.127 (6)	C(8)–C(9)	1.511 (10)	C(17)–C(3)	1.425 (8)
Fe–C(14)	2.057 (7)	C(9)–C(10)	1.333 (9)	C(17)–C(8)	1.525 (8)
Fe–C(17)	2.127 (6)	C(10)–C(11)	1.450 (12)	O(3)–C(18)	1.435 (7)
C(1)–C(2)	1.351 (11)	C(11)–C(12)	1.319 (12)	C(18)–C(19)	1.485 (7)
C(2)–C(3)	1.473 (8)	C(12)–C(13)	1.477 (9)		

C(15)–Fe–C(16)	92.4 (3)	C(3)–Fe–C(14)	124.6 (3)	Fe–C(4)–C(5)	121.7 (4)
C(15)–Fe–C(17)	102.5 (2)	C(3)–Fe–C(13)	128.9 (2)	C(7)–C(14)–C(13)	127.8 (5)
C(15)–Fe–C(7)	157.7 (3)	C(4)–Fe–C(14)	119.7 (2)	C(7)–C(14)–Fe	75.4 (4)
C(15)–Fe–C(3)	94.1 (2)	C(4)–Fe–C(13)	152.6 (3)	C(13)–C(14)–Fe	72.9 (4)
C(15)–Fe–C(4)	112.5 (2)	C(14)–Fe–C(13)	39.6 (2)	C(14)–C(13)–Fe	67.5 (4)
C(15)–Fe–C(14)	127.6 (3)	C(3)–C(17)–Fe	71.4 (3)	C(14)–C(13)–C(12)	130.6 (7)
C(15)–Fe–C(13)	89.5 (3)	C(3)–C(17)–O(3)	115.2 (4)	Fe–C(13)–C(12)	116.8 (4)
C(16)–Fe–C(17)	157.2 (2)	C(3)–C(17)–C(8)	120.1 (4)	C(18)–O(3)–C(17)	111.7 (4)
C(16)–Fe–C(7)	103.2 (2)	Fe–C(17)–O(3)	128.8 (3)	C(11)–C(12)–C(13)	133.1 (6)
C(16)–Fe–C(3)	123.9 (2)	Fe–C(17)–C(8)	94.9 (3)	C(8)–C(9)–C(10)	129.1 (7)
C(16)–Fe–C(4)	89.3 (2)	O(3)–C(17)–C(8)	117.9 (5)	Fe–C(15)–O(1)	175.4 (5)
C(16)–Fe–C(14)	92.6 (3)	C(14)–C(7)–Fe	67.2 (4)	C(6)–C(5)–C(4)	119.9 (6)
C(16)–Fe–C(13)	106.7 (2)	C(14)–C(7)–C(8)	124.1 (5)	C(9)–C(8)–C(17)	116.6 (4)
C(17)–Fe–C(7)	68.1 (2)	Fe–C(7)–C(8)	93.5 (3)	C(9)–C(8)–C(7)	111.0 (5)
C(17)–Fe–C(3)	38.9 (2)	C(17)–C(3)–C(4)	121.9 (5)	C(17)–C(8)–C(7)	103.5 (3)
C(17)–Fe–C(4)	69.3 (2)	C(17)–C(3)–Fe	69.7 (3)	O(3)–C(18)–C(19)	109.2 (5)
C(17)–Fe–C(14)	91.8 (3)	C(17)–C(3)–C(2)	121.4 (5)	C(1)–C(2)–C(3)	121.7 (6)
C(17)Fe–C(13)	90.7 (2)	C(4)–C(3)–Fe	75.3 (3)	C(2)–C(1)–C(6)	120.2 (7)
C(7)–Fe–C(3)	90.3 (2)	C(4)–C(3)–C(2)	116.0 (6)	C(5)–C(6)–C(1)	121.0 (8)
C(9)–Fe–C(4)	83.9 (2)	Fe–C(3)–C(2)	119.5 (4)	C(12)–C(11)–C(10)	129.3 (6)
C(7)–Fe–C(14)	37.3 (3)	C(3)–C(4)–Fe	66.9 (3)	C(9)–C(10)–C(11)	128.6 (8)
C(7)–Fe–C(13)	71.0 (2)	C(3)–C(4)–C(5)	121.1 (5)	Fe–C(16)–O(2)	176.6 (5)
C(3)–Fe–C(4)	37.7 (2)				

Table XI. Bond Lengths (Å) and Bond Angles (deg) of IIIb

Fe–C(19)	1.762 (4)	C(4)–C(5)	1.412 (5)	C(14)–C(7)	1.517 (5)
Fe–C(20)	1.776 (4)	C(5)–C(6)	1.351 (5)	C(7)–C(15)	1.551 (5)
Fe–C(1)	2.231 (3)	C(6)–C(1)	1.427 (5)	C(12)–C(15)	1.533 (4)
Fe–C(2)	2.316 (3)	C(7)–C(8)	1.523 (5)	C(1)–C(15)	1.514 (5)
Fe–C(8)	2.127 (4)	C(8)–C(9)	1.403 (5)	C(15)–O(3)	1.435 (4)
Fe–C(9)	2.049 (5)	C(9)–C(10)	1.395 (6)	O(3)–C(17)	1.424 (5)
Fe–C(10)	2.061 (4)	C(10)–C(11)	1.414 (5)	C(17)–C(18)	1.463 (6)
Fe–C(11)	2.200 (3)	C(11)–C(12)	1.516 (4)	C(4)–C(16)	1.507 (6)
C(1)–C(2)	1.402 (4)	C(12)–C(13)	1.502 (6)	C(19)–O(1)	1.147 (5)
C(2)–C(3)	1.418 (5)	C(13)–C(14)	1.300 (6)	C(20)–O(2)	1.147 (4)
C(3)–C(4)	1.360 (6)				

C(19)–Fe–C(20)	89.4 (2)	C(11)–Fe–C(9)	70.3 (1)	C(10)–C(9)–C(8)	122.3 (4)
C(19)–Fe–C(2)	104.3 (1)	C(11)–Fe–C(8)	83.4 (1)	C(10)–C(9)–Fe	70.6 (3)
C(19)–Fe–C(1)	100.9 (2)	C(9)–Fe–C(8)	39.2 (1)	C(8)–C(9)–Fe	73.4 (3)
C(19)–Fe–C(10)	99.8 (2)	C(1)–C(2)–C(3)	120.6 (3)	C(11)–C(10)–C(9)	121.3 (3)
C(19)–Fe–C(11)	91.2 (1)	C(1)–C(2)–Fe	68.8 (2)	C(11)–C(10)–Fe	76.0 (2)
C(19)–Fe–C(9)	132.0 (2)	C(3)–C(2)–Fe	115.8 (2)	C(9)–C(10)–Fe	69.7 (2)
C(19)–Fe–C(8)	171.0 (2)	C(2)–C(1)–C(15)	123.4 (3)	C(10)–C(11)–C(12)	127.0 (4)
C(20)–Fe–C(2)	88.6 (1)	C(2)–C(1)–C(6)	116.1 (3)	C(10)–C(11)–Fe	65.4 (2)
C(20)–Fe–C(1)	124.4 (1)	C(2)–C(1)–Fe	75.4 (2)	C(12)–C(11)–Fe	111.3 (2)
C(20)–Fe–C(10)	121.7 (2)	C(15)–C(1)–C(6)	118.5 (3)	C(13)–C(12)–C(15)	101.9 (3)
C(20)–Fe–C(11)	159.9 (2)	C(15)–C(1)–Fe	97.1 (2)	C(13)–C(12)–C(11)	113.7 (3)
C(20)–Fe–C(9)	94.7 (2)	C(6)–C(1)–Fe	111.9 (2)	C(15)–C(12)–C(11)	107.6 (3)
C(20)–Fe–C(8)	93.2 (2)	C(2)–C(3)–C(4)	121.8 (3)	C(12)–C(13)–C(14)	110.9 (3)
C(2)–Fe–C(1)	35.9 (1)	C(3)–C(4)–C(5)	118.0 (3)	C(13)–C(14)–C(7)	110.3 (4)
C(2)–Fe–C(10)	141.3 (1)	C(3)–C(4)–C(16)	121.8 (3)	O(3)–C(15)–C(1)	111.0 (3)
C(2)–Fe–C(11)	110.6 (1)	C(5)–C(4)–C(16)	120.2 (4)	O(3)–C(15)–C(7)	111.0 (3)
C(2)–Fe–C(9)	123.5 (1)	C(6)–C(5)–C(4)	121.3 (3)	C(1)–C(15)–C(7)	116.2 (3)
C(2)–Fe–C(8)	84.3 (1)	C(1)–C(6)–C(5)	122.3 (3)	C(18)–C(17)–O(3)	109.4 (4)
C(1)–Fe–C(10)	110.2 (1)	C(15)–C(7)–C(8)	111.9 (3)	Fe–C(19)–O(1)	178.7 (4)
C(1)–Fe–C(11)	75.1 (1)	C(15)–C(17)–C(14)	100.6 (3)	Fe–C(19)–O(2)	117.7 (3)
C(1)–Fe–C(9)	115.2 (1)	C(8)–C(7)–C(14)	110.5 (3)	C(12)–C(15)–O(3)	107.2 (2)
C(1)–Fe–C(8)	84.7 (1)	C(7)–C(8)–C(9)	127.3 (3)	C(12)–C(15)–C(7)	100.1 (3)
C(10)–Fe–C(11)	38.6 (1)	C(7)–C(8)–Fe	108.8 (3)	C(7)–C(15)–C(1)	110.4 (3)
C(10)–Fe–C(9)	39.7 (2)	C(9)–C(8)–Fe	67.4 (2)	C(15)–O(3)–C(17)	116.2 (3)
C(10)–Fe–C(8)	71.6 (2)				

5. $C_8H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3$-*p* (IIIb) and $C_8H_9(CO)_3FeC_6H_4CH_3$-*p* (IVb). (1) Alkylation in CH_2Cl_2 at −60 °C. IIIb and IVb. I (0.5 g, 2.0 mmol) reacted in a similar manner as shown in (1) with 2.0 mmol of $LiC_6H_4CH_3$-*p*.[9] Alkylation and subsequent treatment in a manner similar to that described in (2) gave orange-red crystals of IIIb and light yellow needles of IVb. IIIb: mp 84 °C dec; yield 0.31 g (45%, based on I). Anal. Calcd for $C_{20}H_{20}O_3Fe$ (364.23): C, 65.95; H, 5.54; Fe, 15.33; mol

Table XII. Bond Lengths (Å) and Angles (deg) of IIIc

Fe–C(1)	1.814 (10)	C(6)–C(7)	1.488 (14)
Fe–C(2)	1.782 (9)	C(6)–C(11)	1.429 (14)
Fe–C(5)	2.102 (10)	C(7)–C(8)	1.455 (15)
Fe–C(6)	2.141 (10)	C(8)–C(9)	1.298 (18)
Fe–C(7)	2.264 (11)	C(9)–C(10)	1.444 (16)
Fe–C(14)	2.161 (10)	C(10)–C(11)	1.353 (14)
Fe–C(15)	2.104 (15)	C(11)–C(12)	1.504 (14)
Fe–C(16)	2.200 (11)	C(13)–C(14)	1.491 (16)
O(1)–C(1)	1.148 (13)	C(13)–C(20)	1.541 (15)
O(2)–C(2)	1.143 (12)	C(14)–C(15)	1.319 (18)
O(3)–C(3)	1.468 (14)	C(15)–C(16)	1.480 (20)
O(3)–C(5)	1.395 (14)	C(16)–C(17)	1.465 (19)
C(3)–C(4)	1.511 (15)	C(17)–C(18)	1.382 (19)
C(5)–C(6)	1.470 (13)	C(18)–C(19)	1.399 (17)
C(5)–C(13)	1.554 (14)	C(19)–C(20)	1.347 (17)
C(13)–C(14)–C(15)	128.2 (10)	C(20)–C(13)–C(14)	107.8 (10)
C(14)–C(15)–C(16)	126.7 (11)	C(5)–C(13)–C(14)	104.3 (8)
C(15)–C(16)–C(17)	133.0 (11)	C(5)–C(13)–C(20)	116.3 (8)
C(16)–C(17)–C(18)	128.6 (13)	C(6)–C(5)–C(13)	120.4 (8)
C(17)–C(18)–C(19)	130.7 (12)	O(3)–C(5)–C(6)	116.6 (8)
C(18)–C(19)–C(20)	132.5 (11)	O(3)–C(5)–C(13)	116.6 (8)
C(19)–C(20)–C(13)	127.0 (10)		

Table XIII. Bond Lengths (Å) and Angles (deg) of IVa

Fe–C(1)	1.785 (12)	C(7)–C(8)	1.377 (16)
Fe–C(2)	1.823 (12)	C(8)–C(9)	1.384 (19)
Fe–C(3)	1.760 (10)	C(9)–C(10)	1.356 (16)
Fe–C(6)	2.083 (10)	C(10)–C(11)	1.385 (15)
Fe–C(14)	2.214 (9)	C(13)–C(14)	1.471 (13)
Fe–C(15)	2.089 (10)	C(13)–C(20)	1.323 (13)
Fe–C(16)	2.215 (11)	C(14)–C(15)	1.406 (15)
O(1)–C(1)	1.152 (14)	C(15)–C(16)	1.419 (15)
O(2)–C(2)	1.144 (14)	C(16)–C(17)	1.443 (15)
O(3)–C(3)	1.157 (12)	C(17)–C(18)	1.326 (16)
C(6)–C(7)	1.378 (15)	C(18)–C(19)	1.507 (14)
C(6)–C(11)	1.383 (16)	C(19)–C(20)	1.491 (13)
C(13)–C(14)–C(15)	130.8 (9)	C(17)–C(18)–C(19)	124.3 (9)
C(14)–C(15)–C(16)	120.7 (9)	C(18)–C(19)–C(20)	112.2 (8)
C(15)–C(16)–C(17)	130.3 (9)	C(19)–C(20)–C(13)	125.5 (9)
C(16)–C(17)–C(18)	126.8 (10)	C(20)–C(13)–C(14)	125.2 (9)

wt, 364 (mass spectrum). Found: C, 66.04; H, 5.75; Fe, 15.28. IVb: mp 55 °C dec; yield 0.10 g (15%, based on I). Anal. Calcd for $C_{18}H_{16}O_3Fe$ (336.17): C, 64.31; H, 4.79; Fe, 16.61; mol wt, 336 (mass spectrum). Found: C, 64.70; H, 4.84; Fe, 16.82.

(2) Alkylation in Water at 0 °C. IVb. I (1.0 g, 4.0 mmol) reacted with 4.0 mmol of $LiC_6H_4CH_3$-*p* in a similar manner as described in (1). Alkylation and subsequent treatment in a similar manner as described in (4) gave 0.86 g (63%, based on I) of light yellow needles IVb, mp 55–56 °C dec. Anal. Calcd for $C_{18}H_{16}O_3Fe$ (336.17): C, 64.31; H, 4.79; Fe, 16.61; mol wt, 336 (mass spectrum). Found: C, 64.11; H, 4.92; Fe, 16.28.

6. $C_8H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3$-*o* (IIIc) and $C_8H_9(CO)_3FeC_6H_4CH_3$-*o* (IVc). I (0.5 g, 2.0 mmol) in 100 mL of ether reacted in manner similar to that described in (1) with 2.0 mmol of $LiC_6H_4CH_3$-*o*[9] at −100 °C. The alkylation in CH_2Cl_2 at −60 °C and subsequent treatment in a similar manner as described in (2) or alkylation in H_2O at 0 °C and subsequent treatment in a similar manner as described in (4) gave red crystals of IIIc and yellow needles of IVc. IIIc: mp 93–94 °C dec; yield 0.45 g (60%, based on I). Anal. Calcd for $C_{20}H_{20}O_3Fe$ (364.23): C, 65.95; H, 5.54; Fe, 15.33; mol wt, 364 (mass spectrum). Found: C, 66.13; H, 5.78; Fe, 15.38. IVc: mp 54 °C dec; yield 0.13 g (17%, based on I). Anal. Calcd for $C_{18}H_{16}O_3Fe$ (336.17): C, 64.31; H, 4.79; Fe, 16.61; mol wt, 336 (mass spectrum). Found: C, 64.30; H, 4.79; Fe, 16.68.

7. $C_8H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3$-*m* (IIId) and $C_8H_9(CO)_3FeC_6H_4CH_3$-*m* (IVd). (1) Alkylation in CH_2Cl_2 at −60 °C. IIId and IVd. I (0.5 g, 2.0 mmol) and 2.0 mmol of $LiC_6H_4CH_3$-*m*[9] were used for reaction in a manner similar to that described in (1). Subsequent alkylation and further treatment in a similar manner as described in (2) gave red crystals of IIId and yellow crystals of IVd. IIId: mp 75–76 °C dec; yield 0.28 g (38%, based on I). Anal. Calcd for $C_{20}H_{20}O_3Fe$ (364.23): C, 65.95; H, 5.54; Fe, 15.33; mol wt, 364 (mass spectrum). Found: C, 66.01; H, 5.88; Fe, 15.58. IVd: mp 49 °C dec; yield 0.07 g (10%, based on I). Anal. Calcd for $C_{18}H_{16}O_3Fe$ (336.17): C, 64.31; H, 4.79; Fe, 16.61; mol wt, 336 (mass spectrum). Found: C, 64.70; H, 4.79; Fe, 16.86.

(2) Alkylation in CH_2Cl_2 at −30 °C. IVd. Reaction of 0.50 g (2.0 mmol) of I with 2.0 mmol of $LiC_6H_4CH_3$-*m* in a manner similar to that described in (1) and alkylation in CH_2Cl_2 at −30 °C in a similar manner as described in (2) gave 0.29 g (42%, based on I) of yellow needles of IVd, mp 49 °C dec. Anal. Calcd for $C_{18}H_{16}O_3Fe$ (336.17): C, 64.31; H, 4.79; Fe, 16.61; mol wt, 336 (mass spectrum). Found: C, 64.75; H, 4.67; Fe, 16.35.

(3) Alkylation in Water at 0 °C. IVd. Similar to the procedure described in (1), 0.50 g (2.0 mmol) of I reacted with 2.0 mmol of $LiC_6H_4CH_3$-*m*. The alkylation and subsequent treatment in a similar manner as described in (4) gave 0.39 g (60%, based on I) of yellow needles of IVd, mp 49 °C dec. Anal. Calcd for

Table XIV. Bond Lengths (Å) and Bond Angles (deg) of IVe

Fe–C(12)	2.208 (5)	C(1)–F(1)	1.208 (9)	C(12)–C(13)	1.467 (7)
Fe–C(11)	2.098 (5)	C(1)–F(3)	1.281 (9)	C(7)–C(2)	1.385 (8)
Fe–C(5)	2.065 (5)	C(17)–C(18)	1.474 (8)	C(2)–C(3)	1.384 (8)
Fe–C(18)	2.189 (6)	C(15)–C(16)	1.492 (9)	C(5)–C(8)	1.390 (7)
O(1)–C(8)	1.143 (6)	C(13)–C(14)	1.312 (8)	C(3)–C(4)	1.373 (9)
C(12)–C(11)	1.404 (7)	Fe–C(10)	1.833 (7)	C(1)–F(2)	1.263 (12)
C(11)–C(18)	1.407 (7)	Fe–C(8)	1.787 (5)	C(17)–C(16)	1.334 (8)
C(7)–C(6)	1.376 (8)	Fe–C(9)	1.789 (6)	C(18)–C(17)	1.474 (8)
C(2)–C(1)	1.477 (10)	O(2)–C(9)	1.145 (7)	C(15)–C(14)	1.490 (10)
C(5)–C(4)	1.382 (8)	O(3)–C(10)	1.132 (8)	C(14)–C(13)	1.311 (8)
C(12)–Fe–C(10)	89.4 (2)	C(7)–C(6)–C(5)	122.9 (5)	C(5)–Fe–C(18)	93.9 (2)
C(10)–Fe–C(11)	106.0 (2)	C(2)–C(3)–C(4)	120.4 (5)	Fe–C(12)–C(11)	66.8 (3)
C(10)–Fe–C(8)	90.6 (3)	C(2)–C(1)–F(1)	119.1 (8)	C(11)–C(12)–C(13)	129.3 (5)
C(12)–Fe–C(5)	95.8 (2)	F(1)–C(1)–F(2)	105.8 (9)	Fe–C(11)–C(12)	75.3 (3)
C(11)–Fe–C(5)	79.7 (2)	F(1)–C(1)–F(3)	106.2 (7)	C(12)–C(11)–C(18)	127.1 (5)
C(12)–Fe–C(9)	94.1 (2)	C(16)–C(17)–C(18)	126.4 (6)	Fe–C(8)–O(1)	177.8 (5)
C(11)–Fe–C(9)	126.5 (2)	Fe–C(19)–C(17)	116.0 (5)	C(7)–C(2)–C(1)	122.3 (5)
C(5)–Fe–C(9)	86.1 (2)	C(16)–C(15)–C(14)	111.9 (6)	Fe–C(5)–C(6)	122.5 (4)
C(10)–Fe–C(18)	90.1 (3)	C(17)–C(16)–C(15)	124.8 (6)	C(6)–C(5)–C(4)	115.6 (5)
C(8)–Fe–C(18)	96.4 (2)	C(12)–Fe–C(11)	37.9 (2)	Fe–C(9)–O(2)	178.8 (4)
C(9)–Fe–C(18)	163.9 (2)	C(12)–Fe–C(8)	166.2 (2)	C(5)–C(4)–C(3)	122.7 (5)
Fe–C(12)–C(13)	114.0 (4)	C(11)–Fe–C(8)	129.5 (2)	C(2)–C(1)–F(2)	112.6 (6)
Fe–C(10)–O(3)	174.0 (5)	C(10)–Fe–C(5e	174.3 (2)	C(2)–C(1)–F(3)	113.6 (7)
Fe–C(11)–C(18)	74.3 (3)	C(8)–Fe–C(5)	84.9 (2)	F(2)–C(1)–F(3)	97.0 (7)
C(2)–C(7)–C(6)	119.8 (5)	C(10)–Fe–C(9)	91.2 (3)	Fe–C(18)–C(11)	67.4 (3)
C(7)–C(2)–C(3)	118.4 (6)	C(8)–Fe–C(9)	99.7 (2)	C(11)–C(18)–C(17)	129.4 (4)
C(3)–C(2)–C(1)	119.3 (5)	C(12)–Fe–C(18)	69.9 (2)	C(12)–C(13)–C(14)	126.0 (6)
Fe–C(5)–C(4)	121.7 (3)	C(11)–Fe–C(18)	38.3 (2)	C(15)–C(14)–C(13)	125.9 (6)

$C_{18}H_{16}O_3Fe$ (336.17): C, 64.31; H, 4.79; Fe, 16.61, mol wt, 336 (mass spectrum). Found: C, 64.08; H, 4.82; Fe, 16.83.

8. $C_8H_9(CO)_3FeC_6H_4CF_3$-*p* (IVe). (1) Alkylation in CH_2Cl_2 at −60 °C. I (0.50 g, 2.0 mmol) reacted in a manner similar to that described in (1) with fresh $LiC_6H_4CF_3$-*p*[10] prepared by reaction of 0.46 g (2.0 mmol) of *p*-$CF_3C_6H_4Br$ with 2.0 mmol of *n*-C_4H_9Li.[11] Alkylation and further treatment in a similar manner as described in (2) gave 0.36 g (45%, based on I) of orange needles of IVe, mp 76 °C dec. Anal. Calcd for $C_{18}H_{13}O_3F_3Fe$ (390.14): C, 55.41; H, 3.36; F, 14.61; Fe, 14.31; mol wt, 390 (mass spectrum). Found: C, 55.57; H, 3.22; F, 14.22; Fe, 14.12.

(2) Alkylation in Water at 0 °C. I (1.0 g, 4.0 mmol) reacted in a similar manner as described in (1) with 4.0 mmol of $LiC_6H_4CF_3$-*p*. Subsequent alkylation and further treatment in a similar manner as described in (4) gave 0.53 g (66%, based on I) of orange needles of IVe, mp 74–75 °C dec. Anal. Calcd for $C_{18}H_{13}O_3F_3Fe$ (390.14): C, 55.41; H, 3.36; F, 14.61; Fe, 14.31; mol wt, 390 (mass spectrum). Found: C, 55.62; H, 3.55; F, 15.08; Fe, 14.16.

9. $C_8H_9(CO)_3FeC_6Cl_5$ (IVf). (1) Alkylation in CH_2Cl_2 at −60 °C. I (0.62 g, 2.5 mmol) reacted with fresh solution of LiC_6Cl_5[12] prepared by reaction of 0.90 g (3.2 mmol) of C_6Cl_6 in 50 mL of ether with 3.2 mmol of *n*-C_4H_9Li at −15 °C, in a similar manner as described in (1). Alkylation and further treatment in a similar manner described in (2) and recrystallization from pentane/CH_2Cl_2 at −80 °C gave 0.62 g (51%, based on I) of yellow crystals of IVf, mp 95 °C dec. Anal. Calcd for $C_{17}H_9O_3Cl_5Fe$ (494.37): C, 41.30; H, 1.84; Cl, 35.86; Fe, 11.30; mol wt, 492 (mass spectrum). Found: C, 41.33; H, 2.06; Cl, 36.40; Fe, 11.27.

(2) Alkylation in Water at 0 °C. I (0.50 g, 2.0 mmol) reacted in a manner similar to that described in (1) with ether solution of LiC_6Cl_5 prepared by reaction of 0.73 g (2.5 mmol) of C_6Cl_6 with 2.5 mmol of *n*-C_4H_9Li in ether at −15 °C. Alkylation and further treatment in a similar manner as described in (4) gave 0.58 g (57%, based on I) of yellow crystals of IVf, mp 94–95 °C dec. Anal. Calcd for $C_{17}H_9O_3Cl_5Fe$ (494.37): C, 41.30; H, 1.84; Cl, 35.84; Fe, 11.30; mol wt, 492 (mass spectrum). Found: C, 41.36; H, 2.03; Cl, 36.04; Fe, 11.14.

Crystal Structure Determination. Single crystals of complexes IIIa–c, IVa, and IVe were obtained by recrystallization from pentane solution at −80 °C. The single crystals were sealed in capillaries under N_2 atmosphere. X-ray diffraction data were collected by using Syntex R3 four-circle diffractometer at 20–22 °C. All except IVa showed no obvious decay during the data collection. The crystallographic data for the five crystals, experimental conditions of collecting data, and final discrepancy index etc. are listed in Table VI.

After correction for the *Lp* factor and the empirical absorption factor, the intensity data of IIIa and IIIb were placed on an approximately absolute scale by the Wilson statistical method. The structure of IIIa was solved by Patterson–Fourier techniques providing the positional parameters of the Fe atom; the other non-hydrogen atoms were derived from difference Fourier syntheses. The structure of IIIb was solved by direct methods. The positional parameters of 22 non-hydrogen atoms were located by difference Fourier techniques and refined with the anisotropic thermal parameters. All hydrogen atoms were obtained from a *D* map; the positional parameters of the hydrogen atoms of the ethyl group of IIIa could not be converged and were placed in idealized positions.

Intensity data for IIIc were empirically corrected for absorption. The structure was solved by the Patterson method. Because the Fe atom located at $z = {}^1/_2$ in crystal IIIc, double solutions of the phases could be derived in the Fourier synthesis. The phases were derived by choosing those atoms from the electron density map which belonged to the same set.

Because crystals of IVa decayed rapidly under X-ray irradiation, the collection of data was completed with five crystals. All data were unified to a common scale with the same selected standard reflections. No correction for absorption was made. The positional parameters of the Fe atom were derived by the Patterson method, and the other non-hydrogen atoms were obtained from Fourier synthesis. The structure was refined to convergence by block-matrix least squares.

The positional parameters of the Fe atom for IVe was obtained by the Patterson method, and the other non-hydrogen atoms were derived from the difference Fourier function. All hydrogen atoms were obtained from a *D* map.

The fractional coordinates and equivalent temperature factors of the non-hydrogen atoms for IIIa–c, IVa, and IVe are listed in Tables VII–IX, respectively. Bond lengths and angles for IIIa–c, IVa, and IVe are given in Tables X–XIV, respectively. Computations were performed by using SHELXTL programs (Nicolet Corp., Madison, WI).

Because the structure factor data for crystals IIIa–c, IVa, and IVe recorded on magnetic tape were all destroyed due to an unforeseen accident, we have now only the original intensity data for crystals IIIa, IIIb, and IVa. The intensity data for crystals IIIc and IVe were also lost by accident, so only their final structural data can be provided.

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Registry No. I, 12093-05-9; IIIa, 110096-61-2; IIIb, 110141-89-4; IIIc, 110096-63-4; IIId, 110096-67-8; IVa, 110096-62-3; IVb, 110096-65-6; IVc, 110096-66-7; IVd, 110096-68-9; IVe, 110096-64-5; IVf, 110096-69-0; $C_8H_8(CO)_2FeC(OLi)C_6H_5$, 110096-70-3; LiC_6H_5, 591-51-5; $LiC_6H_4CH_3$-*p*, 2417-95-0; $LiC_6H_4CH_3$-*o*, 6699-93-0; $LiC_6H_4CH_3$-*m*, 10325-82-3; $LiC_6H_4CF_3$-*p*, 2786-01-8; LiC_6Cl_5, 6782-80-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen coordinates, least-squares refinement, nonbonded distances, and bond distances and angles for IIIc and IVe and torsional angles for IIIc (19 pages); listings of structure factors for IIIc and IVe (2 pages). Ordering information is given on any current masthead page.