

SYNTHESIS AND CRYSTAL STRUCTURE OF ISOMERIZED BUTADIENE(DICARBONYL)(ETHOXYARYLCARBENE)IRON COMPLEXES *

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Summary

Reaction of π -butadienetricarbonyliron(I) with aryllithium ArLi (Ar = phenyl, substituted phenyl, 1-naphthyl and 2-thienyl) in ether at low temperature, followed by the alkylation of the acylmetallate obtained with triethyloxonium tetrafluoroborate $[(C_2H_5)_3OBF_4]$ in water solution at 0°C gave 10 orange-red crystalline complexes with the composition $C_4H_6(CO)_2FeC(OC_2H_5)Ar$. On the basis of elemental analyses, IR, 1H NMR and mass spectra, as well as single crystal X-ray structure determination, it is corroborated that these new compounds were isomers of butadienyldicarbonyl(ethoxyarylcabene)iron complexes with two types of structure. A possible reaction mechanism is tentatively proposed and discussed in this paper.

Introduction

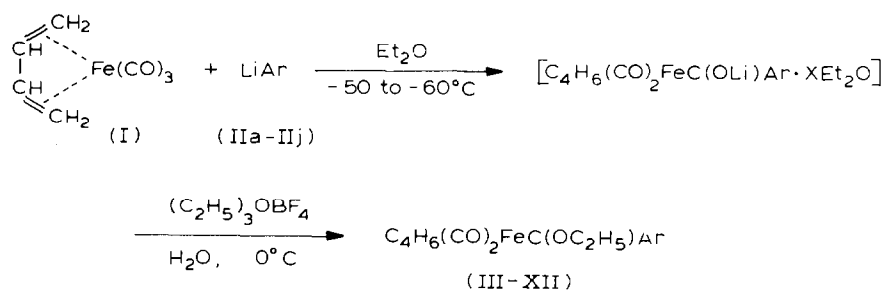
Since 1964, a large number of transition metal carbene complexes have been synthesized and characterized by Fischer et al. [1–3]. Up to now, there are only a few examples of metal carbene complexes in which the metal is bonded to an olefin and a carbene ligand [4a,b,c]. However, the synthesis of a π -olefin transition metal carbene complex directly from a π -olefin metal carbonyl compound has not yet been reported. The synthesis of such a carbene complex would permit the study of the effect of the olefin ligand on the chemistry of the carbene ligand and the reactivity of the π -olefin ligand. An attempt was made at synthesizing the butadiene(dicarbonyl)(ethoxyarylcabene)iron complexes by the reactions of butadienetri-

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carbonyliron(I) with aryllithium followed by alkylation of the acylmetallates obtained.

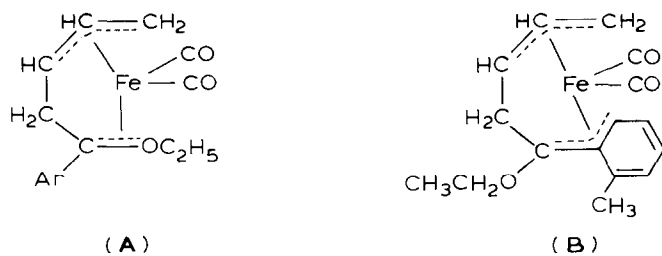
Preparative results

Similar to the preparation of general alkoxy carbene complexes [5,6], equimolar quantities of I and aryllithium, LiAr (Ar = phenyl, substituted phenyl, 1-naphthyl and 2-thienyl), were used for the reaction in diethyl ether at low temperature, and the acylmetallate compounds produced were alkylated with triethyloxonium tetrafluoroborate, $(C_2H_5)_3OBF_4$, in water at $0^\circ C$. The reaction products were chromatographed on an alumina column at low temperature and recrystallized from pentane solution at $-80^\circ C$ to give orange-red crystalline compounds III–XII with general composition $C_4H_6(CO)_2FeC(OC_2H_5)Ar$. The reactivities and yields of the resulting compounds were dependent on the nucleophiles used. Thus IIc, Iii and Iij gave relatively low yields, while others gave moderate yields. Unexpectedly, when R of LiR is alkyl, diethylamino, α -phenylacetylenyl or benzyl, no analogous products were obtained under the same conditions.



Complex	Ar	Complex	Ar
IIa \rightarrow III	C_6H_5	IIf \rightarrow VIII	<i>p</i> -Cl C_6H_4
IIb \rightarrow IV	<i>p</i> -CH $_3C_6H_4$	IIg \rightarrow IX	<i>m</i> -Cl C_6H_4
IIc \rightarrow V	<i>o</i> -CH $_3C_6H_4$	IIh \rightarrow X	<i>p</i> -CF $_3C_6H_4$
II d \rightarrow VI	<i>m</i> -CH $_3C_6H_4$	IIi \rightarrow XI	α -C $_{10}H_7$
IIe \rightarrow VII	<i>p</i> -CH $_3OC_6H_4$	IIj \rightarrow XII	2-C $_4H_3S$

The diamagnetic complexes III–XII were readily soluble both in polar and non-polar solvents and were highly sensitive to air and temperature in the solid state, as well as in solution. The crystalline solids decomposed to black powders at room temperature. The intermediates, $C_4H_6(CO)_2FeC(OLi)Ar \cdot XEt_2O$, which were extremely sensitive to air and moisture, decomposed rapidly on exposure to air. On the



basis of elemental analyses, spectral analyses and single crystal X-ray structure determinations, these new compounds are formulated as isomerized butadiene(dicarbonyl)(ethoxyarylcarbene)iron complexes with two types of structure, **A** and **B**, among which complex V exists in the form of structure **B**, while the others exist in the form of structure **A**.

Spectral studies

Infrared spectra. The IR spectra of complexes III–XII and $C_4H_6(CO)_2FeC(OLi)Ar \cdot 2Et_2O$ are given in Table 1. All of these complexes show the two expected stretching vibration bands in the $\nu(CO)$ region in accordance with that of metal carbonyl compounds with general formula $(CO)_2MLL'$.

Table 1 indicates that the various substituents on the phenyl ring had no notable influence on the $\nu(CO)$ frequency. In comparison with complex III, the two $\nu(CO)$ stretching vibrations of $C_4H_6(CO)_2FeC(OLi)C_6H_5 \cdot 2Et_2O$ decreased by about 28 and 100 cm^{-1} , respectively. This was rather consistent with the carbene complex $\pi-C_5H_5(CO)_2ReC(OCH_3)C_6H_5$ and its precursor $\pi-C_5H_5(CO)_2ReC(OLi)C_6H_5$ [7].

1H NMR spectra. The 1H NMR spectra of III–XII in acetone- d_6 at $20^\circ C$ showed two proton signals attributed to ethoxy groups (OCH_2CH_3) from each of the complexes, in addition to the other expected proton signals (Table 2). This may be explained as follows: according to single crystal X-ray structure analyses the C(3)–O(3) bond was a partial double bond, which suggested that there existed, as in $(CO)_5CrC(OCH_3)C_6H_5$ [6], two probable geometrical *cis-trans* isomers (with regard to the C(3)–O(3) bond), arising from difference in arrangement of ethyl and aryl

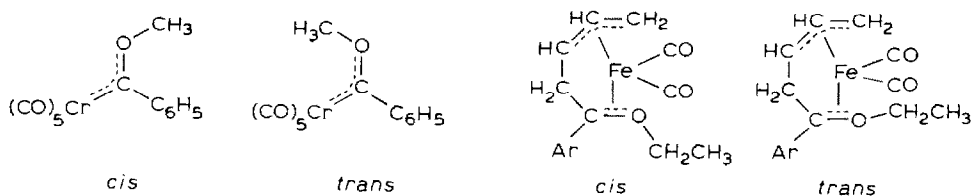
TABLE 1
IR SPECTRA OF THE COMPLEXES III–XII AND $C_4H_6(CO)_2FeC(OLi)C_6H_5 \cdot 2Et_2O$

Complex	$\nu(CO)$ (cm^{-1})				Solvent
$C_4H_6(CO)_2FeC(OLi)C_6H_5 \cdot 2Et_2O$	1950vs			1805vs	CH_2Cl_2
III	1995vs	1975sh	1940sh	1930vs	hexane
	1980vs			1910vs	CH_2Cl_2
IV	1993vs	1982sh	1938sh	1927vs	hexane
	1978vs			1907vs	CH_2Cl_2
V	1997vs	1983sh	1940vs	1908w	hexane
	1983vs			1920vs	CH_2Cl_2
VI	1993vs	1974sh	1940sh	1930vs	hexane
	1980vs			1908vs	CH_2Cl_2
VII	1992vs	1984sh	1938sh	1928vs	hexane
	1976vs			1905vs	CH_2Cl_2
VIII	1996vs	1988sh	1948sh	1933vs	hexane
	1982vs			1912vs	CH_2Cl_2
IX	1998vs	1988sh	1952sh	1934vs	hexane
	1983vs			1913vs	CH_2Cl_2
X	2000vs	1986sh	1952sh	1935vs	hexane
	1985vs			1917vs	CH_2Cl_2
XI	2000vs	1985sh	1945sh	1918vs	hexane
	1986vs			1925vs	CH_2Cl_2
XII	1998vs	1978sh	1943vs	1910w	hexane
	1989vs			1925vs	CH_2Cl_2

TABLE 2
¹H NMR SPECTRA OF THE COMPLEXES III–XII IN ACETONE-*d*₆ AT 20°C (δ(ppm), TMS as internal reference)

Complex	δ(OCH ₂ CH ₃)		Molecular ratio <i>trans/cis</i>	δ(OCH ₂ CH ₃)	δ(CH ₂ =CH=CHCH ₂)	δ(aryl-proton)	δ(CH ₃)	δ(OCH ₃)
	<i>trans</i>	<i>cis</i>						
III	4.60	4.25	0.83	1.43	2.88(m,4)	3.80(m,2)	7.27(m,5)	
IV	4.53	4.19	0.85	1.40	2.84(m,4)	3.76(m,2)	7.14(m,2)	7.08(m,2)
V	5.42	5.09	1.2	1.26	2.91(m,4)	3.68(m,2)	7.44(m,2)	7.20(m,1)
VI	4.56	4.22	0.74	1.42	2.86(m,4)	3.78(m,2)	7.00(m,1)	2.31(m,3)
VII	4.52	4.18	0.76	1.41	2.89(m,4)	3.80(m,2)	7.20(m,2)	6.82(m,2)
VIII	4.60	4.25	0.79	1.42	2.86(m,4)	3.85(m,2)	7.27(m,4)	
IX	4.58	4.27	0.79	1.43	2.83(m,4)	3.85(m,2)	7.23(m,4)	
X	4.66	4.28	0.92	1.44	2.86(m,4)	3.91(m,2)	7.54(m,2)	7.46(m,2)
XI	5.10	4.88	0.80	1.34	2.90(m,4)	3.76(m,2)	7.90(m,2)	7.48(m,5)
XII	5.55	5.05	0.76	1.30	2.87(m,4)	3.85(m,2)	7.29(m,1)	7.07(m,2)

groups. Consequently, environmental effects cause the appearance of two proton signals for the ethoxy methylene hydrogens (OCH_2CH_3).



It can also be seen that as a result of a σ - π rearrangement of the butadiene ligand in all these complexes, their structures consist of a π -allyl and a terminal carbon bonded to the carbene carbon (C(3)). Thus the proton signal of the original olefin ligand shifted accordingly. The resonance peaks for butadiene protons in complex I (δ 5.28, 1.18 and 0.22 ppm) [8] disappeared and two broad peaks (δ 2.8 and 3.8 ppm with intensity ratio 4/2) appeared which could be assigned to four π -allyl protons and to the two protons of the terminal carbon atom, respectively.

Mass spectra. The mass spectra of complexes III–XII provided a series of characteristic ions bearing useful structural information. All of the complexes showed the principal fragments produced by successive loss of CO ligand, and ion peaks from fragmentation of the ethoxy and phenyl bonded to iron atom, as well as their molecular ions. The detailed studies will be described in another report [9].

X-Ray crystallography and the results of structure analysis for IV and V

The single crystals of IV and V were obtained by crystallization from pentane solution at dry ice temperature. The single crystals used were of dimension ~ 0.3 mm and sealed in capillaries under N_2 . Intensity data of 1729 and 1927 independent reflections were collected with a Syntex R_3 four-circle diffractometer using $\text{Mo-K}\alpha$ radiation by $\theta/2$ scan mode ($5^\circ < 2\theta < 43^\circ$) for IV and V, respectively. We used variable scan speeds in the range 4–29.3 min^{-1} and selected the background/scan time ratio of 0.2. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was also applied. Compounds IV and V crystallize in the triclinic system, space group $P\bar{1}$ with $Z = 2$ for $\text{C}_4\text{H}_6(\text{CO})_2\text{-FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3$, and with a 7.850(3), b 10.500(5), c 10.960(5) Å, α 107.04(3), β 105.92(3), γ 107.01(4)°, V 759.2 Å³, D_c 1.37 g/cm^3 for IV and a 8.673(3), b 8.854(3), c 10.977(3) Å, α 91.39(2), β 104.52(2)°, γ 116.72(2)°, V 719.6 Å³, D_c 1.45 g/cm^3 for V.

The structure of IV was solved by Patterson-Fourier techniques, and the structure of V by the direct method using the SHELXTL program. Most of the hydrogen atoms were derived from difference function. The block-diagonal least-squares refinement gave final discrepancy indices $R = 0.0535$ for IV with 1466 reflections and R 0.0567, R_w 0.0429 ($w = 1/[\sigma^2(F) + 0.0001F^2]$) for V with 1517 reflections. The final fractional coordinates and equivalent isotropic temperature factors of non-hydrogen atoms and positional and isotropic parameters for hydrogen atoms are given in Tables 3 and 4, respectively. The molecular structures of complexes IV and V are shown in Fig. 1 and 2, respectively. The selected bond lengths and angles are shown in Table 5. All the anisotropic thermal parameters of non-hydrogen atoms will not be listed owing to limitations of space.

TABLE 3

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\times 10^{-3}$)

Atom	IV				V			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Fe	3973(1)	6521(1)	3002(1)	62(1)	3126(1)	733(1)	2525(1)	34(1)
O(1)	1541(10)	5132(8)	4254(7)	111(5)	5786(5)	-511(5)	3026(4)	72(3)
O(2)	1535(9)	7980(8)	2224(8)	104(5)	3731(5)	1649(5)	96(3)	69(2)
O(3)	6436(5)	8188(4)	4383(4)	64(2)	582(4)	2361(4)	1914(3)	39(2)
C(1)	2493(13)	5650(9)	3754(9)	76(5)	4712(7)	-68(6)	2815(5)	47(3)
C(2)	2565(12)	7461(10)	2583(9)	69(5)	3527(7)	1362(6)	1081(5)	43(3)
C(3)	6492(8)	7777(6)	3049(6)	61(3)	1766(7)	2081(6)	2888(4)	35(3)
C(4)	3058(11)	5232(8)	905(8)	75(4)	515(7)	-1176(7)	1448(6)	52(3)
C(5)	3841(10)	4591(7)	1712(7)	78(4)	1057(7)	-1542(6)	2659(5)	49(3)
C(6)	5729(14)	5279(9)	2733(10)	75(5)	1491(7)	-447(6)	3757(5)	45(3)
C(7)	7203(10)	6574(8)	2701(8)	75(4)	916(7)	885(7)	3765(5)	46(3)
C(8)	7909(10)	8285(10)	5591(8)	80(4)	-376(7)	3108(7)	2339(5)	55(3)
C(9)	7162(13)	8253(11)	6676(9)	86(5)	-1588(8)	3321(9)	1210(6)	76(4)
C(10)	7848(14)	2348(11)	1019(12)	106(7)	3536(7)	5252(7)	1576(5)	59(3)
C(11)	7528(8)	1171(7)	1560(7)	78(4)	7459(8)	5084(7)	3931(6)	54(3)
C(12)	7209(10)	1354(8)	2772(8)	77(4)	6397(7)	5538(7)	2985(5)	49(3)
C(13)	6879(9)	282(7)	3248(7)	71(4)	4558(7)	4687(7)	2625(5)	38(3)
C(14)	6891(8)	8943(7)	2577(7)	60(3)	3656(6)	3260(6)	3255(4)	32(2)
C(15)	7246(9)	8758(8)	1367(7)	74(4)	4782(7)	2840(6)	4216(4)	39(3)
C(16)	7524(10)	9836(8)	886(8)	79(4)	6682(7)	3764(7)	4522(5)	48(3)

^a Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalised U_{ij} 's tensor.

TABLE 4

HYDROGEN COORDINATES ($\times 10^{-3}$) AND TEMPERATURE FACTORS ($\times 10^{-3}$)

Atom	IV				V			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
HC(41)	174(7)	483(5)	40(5)	61(15)	44(7)	-185(7)	74(5)	69(18)
HC(42)	370(7)	588(5)	50(5)	82(14)	-35(8)	-66(7)	127(5)	82(21)
HC(5)	308(8)	367(6)	172(5)	62(17)	112	-260	273	57
HC(6)	620(7)	481(5)	333(5)	62(14)	218	-61	454	53
HC(71)	855(7)	687(5)	342(5)	83(14)	-38	38	347	57
HC(72)	713(8)	639(6)	168(6)	100(19)	135	151	461	57
HC(81)	905(8)	929(6)	597(5)	80(15)	-108	238	284	65
HC(82)	813(7)	738(6)	523(5)	71(16)	46	421	284	65
HC(91)	808(8)	823(6)	756(6)	87(16)	-224	384	146	84
HC(92)	701(9)	921(7)	700(7)	147(22)	-242	218	77	84
HC(93)	603(8)	723(6)	636(6)	111(19)	-94	399	66	84
HC(101)	930	278	125	211(35)	266	547	182	67
HC(102)	703	179	-5	200(34)	294	434	87	67
HC(103)	735	313	147	351(50)	438	627	134	67
HC(11)					875	571	415	69
HC(12)	736(8)	230(6)	329(6)	74(18)	699	649	257	61
HC(13)	696(8)	42(6)	414(6)	50(17)				
HC(15)	712(9)	787(7)	90(7)	83(22)	424	190	465	47
HC(16)	759(7)	972(5)	3(6)	80(15)	742	347	517	58

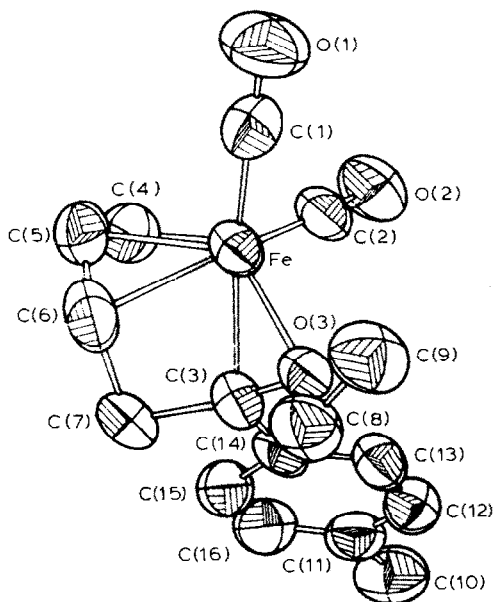


Fig. 1. Molecular structure of IV.

The results of the X-ray structure analyses show that: (i) In the reaction, one π bond of each butadiene molecule has been opened with the aid of iron medium, such that carbon atom C(7) forms a new bond with the "carbene" atom C(3) and leaves the other three carbon atoms C(4), C(5) and C(6) of the butadiene ligand to act as a π -allyl moiety. As shown in Table 5, the distances between the iron atom and C(4),

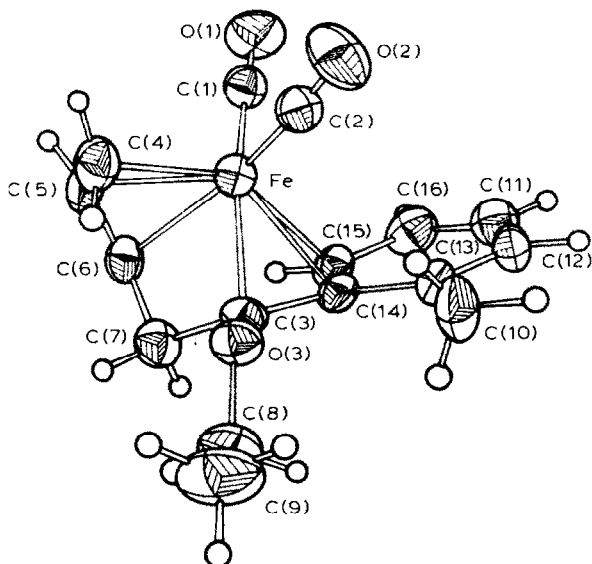
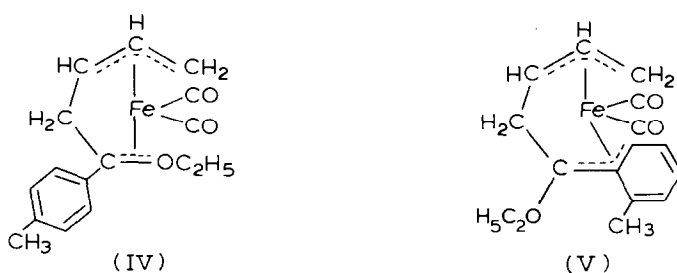


Fig. 2. Molecular structure of V.

TABLE 5
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (deg.)

	IV	V	IV	V	IV	V	IV	V
Fe-C(1)	1.792(11)	1.779(7)	Fe-C(4)	2.081(7)	2.122(5)	Fe-C(14)	2.160(5)	
Fe-C(2)	1.741(11)	1.757(6)	Fe-C(5)	2.057(8)	2.049(5)	Fe-C(15)	2.253(4)	
Fe-C(3)	2.008(6)	2.110(7)	Fe-C(6)	2.176(12)	2.157(6)	Fe-O(3)	1.988(3)	
C(1)-O(1)	1.147(14)	1.140(9)	C(2)-O(2)	1.147(14)	1.155(7)	C(3)-O(3)	1.415(8)	
C(3)-C(8)	1.454(9)	1.420(9)	C(8)-C(9)	1.467(15)	1.488(9)	C(3)-C(14)	1.449(11)	
C(4)-C(5)	1.381(13)	1.392(8)	C(5)-C(6)	1.400(10)	1.372(8)	C(6)-C(7)	1.523(13)	
C(7)-C(3)	1.517(2)	1.515(7)	C(11)-C(12)	1.387(12)	1.401(9)	C(12)-C(13)	1.362(13)	
C(13)-C(14)	1.387(11)	1.453(7)	C(14)-C(15)	1.399(12)	1.427(8)	C(15)-C(16)	1.369(13)	
C(16)-C(11)	1.379(11)	1.337(8)	C(13)-C(10)		1.509(8)	C(11)-C(10)	1.507(16)	
C(1)-Fe-C(2)	94.0(5)	93.1(3)	C(3)-Fe-C(4)	91.4(3)	84.5(2)	C(14)-Fe-C(2)	92.1(2)	
C(1)-Fe-C(3)	153.5(3)	158.8(2)	C(3)-Fe-C(5)	95.5(3)	91.3(2)	C(14)-Fe-C(4)	122.4(3)	
C(1)-Fe-C(4)	110.9(3)	111.6(3)	C(3)-Fe-C(6)	70.1(3)	68.9(2)	C(14)-Fe-C(5)	126.3(2)	
C(1)-Fe-C(5)	93.5(4)	93.3(2)	O(3)-Fe-C(1)	114.2(3)		C(14)-Fe-C(6)	93.0(2)	
C(1)-Fe-C(6)	103.3(5)	103.1(3)	O(3)-Fe-C(2)	99.9(3)		C(15)-Fe-C(1)	92.7(2)	
C(2)-Fe-C(3)	100.3(4)	101.4(3)	O(3)-Fe-C(4)	132.7(2)		C(15)-Fe-C(2)	113.9(2)	
C(2)-Fe-C(4)	90.3(4)	88.0(2)	O(3)-Fe-C(5)	123.7(2)		C(15)-Fe-C(4)	146.8(3)	
C(2)-Fe-C(5)	127.2(3)	124.1(2)	O(3)-Fe-C(6)	86.3(2)		C(15)-Fe-C(5)	121.2(2)	
C(2)-Fe-C(6)	157.5(4)	155.6(2)	C(14)-Fe-C(1)		125.9(2)	C(15)-Fe-C(6)	83.9(2)	
C(4)-C(5)-C(6)	123.3(7)	123.0(6)	O(3)-C(8)-C(9)	110.1(7)	109.0(5)	C(15)-C(16)-C(11)	123.2(8)	
C(5)-C(6)-C(7)	119.3(9)	121.8(5)	C(3)-C(14)-C(13)	123.1(7)	126.4(4)	C(16)-C(11)-C(12)	115.2(8)	
C(6)-C(7)-C(3)	104.7(7)	106.5(5)	C(3)-C(14)-C(15)	121.3(7)	116.1(4)	C(10)-C(11)-C(12)	122.3(8)	
C(7)-C(3)-C(14)	123.1(7)	121.6(4)	C(11)-C(12)-C(13)	122.5(8)	122.7(5)	C(10)-C(11)-C(16)	122.5(8)	
C(7)-C(3)-O(3)	113.4(6)	115.9(4)	C(12)-C(13)-C(14)	122.4(8)	118.9(5)	C(10)-C(13)-C(12)	118.7(5)	
O(3)-C(3)-C(14)	114.7(5)	119.6(4)	C(13)-C(14)-C(15)	115.6(8)	116.8(4)	C(10)-C(13)-C(14)	122.5(4)	
C(3)-O(3)-C(8)	123.2(6)	114.7(4)	C(14)-C(15)-C(16)	121.1(8)	121.0(5)			

C(5) and C(6) vary only slightly from 2.05 to 2.16 Å in molecules IV and V. Owing to the variation of bond type of $\text{Fe}=\text{C}_{\text{carbene}}$, caused by the bonding of C(7) to carbene carbon C(3), the resulting products III–XII (relating to the complexes containing $\text{Fe}=\text{C}_{\text{carbene}}$) may be regarded as isomerized carbenciron complexes. (ii) Very fascinatingly, in molecule IV containing *p*-tolyl which has a smaller steric hindrance, one p_z orbital of O(3) atom coordinates to iron with a pair of electrons, whereas in molecule V containing *o*-tolyl, which has a greater steric hindrance, localized π -molecular orbital composed of C(14) and C(15) in the benzene ring with a pair of π -electrons, should overlap with the orbital of the Fe atom instead, to satisfy the 18-electron rule. According to the data of bond lengths in the benzene ring given in Table 5, the alternately long and short lengths in the benzene ring (C(12)–C(13) 1.36, C(11)–C(16) 1.34, C(11)–C(12) 1.40, C(13)–C(14) 1.43, C(14)–C(15) 1.45, C(15)–C(16) 1.41 Å) were obviously observed. This fact indicates that the benzene ring exhibits slightly localized bonding. In addition, the position of the benzene ring relative to the Fe atom and the dihedral angle between the benzene ring and $\text{Fe}-\text{C}(14)-\text{C}(15)$ (115.2°) in V further supported that the p_z - π molecular orbital composed of C(14) and C(15) in the benzene ring should interact with the orbital of iron. (iii) We noted that the sum of the bond angles C(7)–C(3)–C(14), C(7)–C(3)–O(3) and C(14)–C(3)–O(3) are 351.2 and 357.1° in IV and V, respectively, only slightly deviating from 360° . Thus, it is concluded that the carbene carbon forms three σ bonds to C(7), C(14) and O(3) with sp^2 hybridized orbitals instead of sp^3 hybridized orbitals and provides an approximately pure p_z atomic orbital to interact with iron, in both complexes. Because the p_z orbital of C(3) is almost parallel to that of O(3) in IV or to the two p_z orbitals of C(14) and C(15) in V, a ligand analogous to π -allyl is able to be formed with one electron in the p_z orbital of C(3) and two electrons in the p_z orbital of O(3) in IV, or with one electron in the p_z orbital of C(3) and two electrons in the two p_z orbitals of C(14) and C(15) in V. If iron is regarded as zerovalent, it is reasonable that the π orbital of the ligands composed of three electrons, as depicted above, should further interact with Fe. The corresponding structure of IV and V are given as follows:

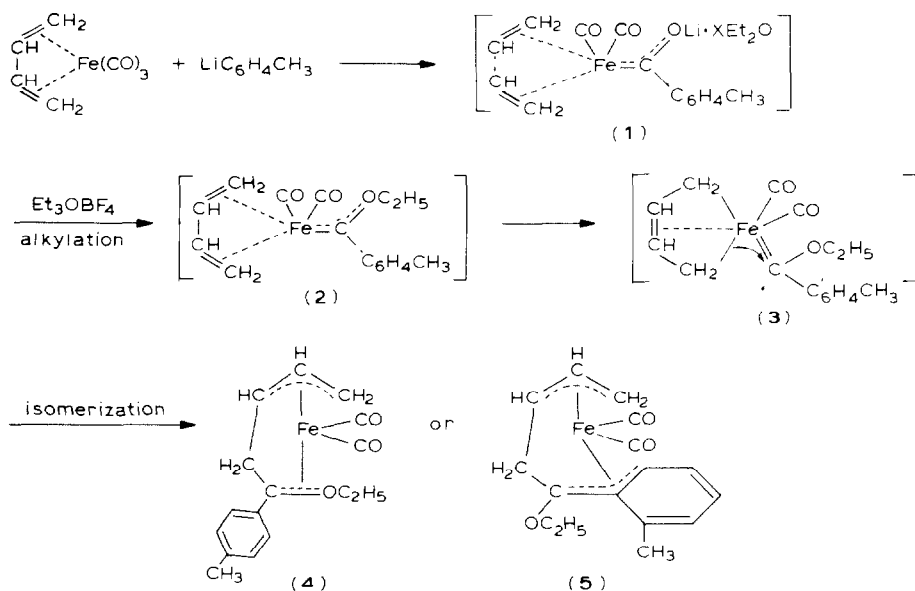


(iv) The fact that the crystal density of V (1.45 g/cm^3) is notably higher than that of complex IV (1.37 g/cm^3) suggests that the structure of complex V is more compact than that of complex IV. The bond type existing in V is novel, and only two examples of the analogous bond type has hitherto been reported by King and others [10a–c]. Further investigations, for example, the calculation of electron densities on ligands and the models of bonded orbital provided by metal atom, will be worthwhile.

Discussion

The reaction of I with aryllithium reagents and subsequent alkylation with $(C_2H_5)_3OBF_4$ yielded isomerized butadiene(dicarbonyl)(ethoxyarylcarbene)iron complexes, instead of normal carbene complexes. It might be supposed that, as shown in Scheme 1, the normal acylcarbonyl lithium compounds **1** were formed when I reacted with aryllithium, and isomerization took place while compounds **1** were alkylated with $(C_2H_5)_3OBF_4$. Thus we observed the formation of acyl metallate compounds which precipitated as a yellow solid from reaction mixtures. In addition we succeeded in obtaining an analytically pure compound **1**. Its composition and structure were supported by the elemental analyses and IR spectra of the intermediate, $C_4H_6(CO)_2Fe(OLi)C_6H_5 \cdot 2(C_2H_5)_2O$. In this manner, we speculate that the possible mechanism of formation of the isomerized carbeneiron complexes may be as shown in Scheme 1. As soon as the ethoxyarylcarbene complexes **2** were formed by alkylation of **1** with $(C_2H_5)_3OBF_4$, rearrangement of π -bonding of the double bonds in butadiene to give an intermediate, metallacycle **3**, which converted to the stable isomerized carbene complexes **4** or **5**. The molecular structures of these

SCHEME 1



isomerized carbene complexes satisfy the 18-electron rule.

Very interestingly, only when the nucleophiles were aryllithium, the reaction of I with nucleophiles can take place to give isomerized carbene complexes. In this way, we assumed that there should be a large conjugated system in the molecules of the resulting products.

The reactivities of these new compounds are under investigation.

Experimental

IR spectra were run on a Perkin-Elmer 683 spectrophotometer, ^1H NMR spectra were measured using a Varian XL-200 spectrometer and mass spectra were recorded using a Finnigan 4021 GC/MS/DS spectrometer.

All operations must be carried out under pre-purified nitrogen. 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 a high vacuum, deactivated with 5% w/w water and stored under N_2 . Butadienetricarbonyliron [11], and the aryllithium reagents used were prepared as described in ref. 12 and refs. 14–19.

1. $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OLi})\text{C}_6\text{H}_5 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$

To a solution of 2.0 g (10.3 mmol) of I in 100 ml of ether was added dropwise 10.3 mmol of LiC_6H_5 [12] in 20 ml of ether at -50°C within 20 min. The yellow precipitate separated out from the mixture. After stirring at -50 to -40°C for 0.5 h, the dark-red solution was decanted. The resulting yellow crystals were washed with ether at 0°C and then dried in a high vacuum at -30°C ; yield 3.6 g (82%, based on I). Found: C, 58.81; H, 7.31; O, 18.48. $\text{C}_{21}\text{H}_{31}\text{O}_5\text{LiFe}$ (426.27) calcd.: C, 59.17; H, 7.33; O, 18.77%.

2. $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5$ (III)

3.0 g of $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OLi})\text{C}_6\text{H}_5 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ was dissolved in 50 ml of N_2 -saturated water at 0°C and covered with pentane. Then $(\text{C}_2\text{H}_5)_3\text{OBF}_4$ [13] was added portionwise with stirring to the water solution until it became acidic. The water solution was extracted with pentane. The pentane extract was dried over anhydrous Na_2SO_4 . After evaporation of solvent in a high vacuum, the residue was submitted to column chromatography on alumina at -20°C with pentane followed by pentane/ether (10/1) as eluent. After the separation of unreacted I from the column the yellow zone was collected. The solvent was removed in a high vacuum and the residue was recrystallized from pentane at -80°C to give orange-red needles, m.p. 59°C (decomp.), yield 1.71 g (81%, from $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OLi})\text{C}_6\text{H}_5 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$) Found: C, 60.01; H, 5.36; O, 16.49; Fe, 18.47. $\text{C}_{15}\text{H}_{16}\text{O}_3\text{Fe}$ (300.14) calcd.: C, 60.03; H, 5.37; O, 16.00; Fe, 18.61%. Mol. wt. 300 (mass spec., based on ^{56}Fe).

3. $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-p}$ (IV)

A solution of 5.2 mmol of $p\text{-CH}_3\text{C}_6\text{H}_4\text{Li}$ [14] in 20 ml of ether was added dropwise, with vigorous stirring, to a solution of 1.0 g (5.2 mmol) of I in 60 ml of ether at -50°C for a period of 20 min. The reaction mixture was stirred at -50°C for 3 h. The solvent was removed in a high vacuum to give a yellow solid residue. Further treatment of the residue in a similar manner as described in 2 and recrystallization from pentane at -80°C gave 0.9 g (56%, based on I) of orange-red needles. m.p. 63°C (decomp.). Found: C, 61.25; H, 5.89; O, 15.30; Fe, 17.47. $\text{C}_{16}\text{H}_{18}\text{O}_3\text{Fe}$ (314.17) calcd.: C, 61.17; H, 5.78; O, 15.28; Fe, 17.78%. Mol. wt. 314 (mass spec.).

4. $\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}$ (V)

Similar to the procedures described in 3, the reaction of 0.7 g (3.6 mmol) of I with 3.6 mmol of $o\text{-CH}_3\text{C}_6\text{H}_4\text{Li}$ [14] for 3 h gave 0.08 g (7.1%, based on I) of orange-red

crystals; m.p. 65°C (decomp.) Found: C, 61.44; H, 5.89; O, 15.08; Fe, 17.42. C₁₆H₁₈O₃Fe (314.17) calcd.: C, 61.17; H, 5.78; O, 15.28; Fe, 17.78%. Mol. wt. 314 (mass spec.).

5. C₄H₆(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*m* (VI)

The reaction of 0.5 g (2.6 mmol) of I with 2.6 mmol of *m*-CH₃C₆H₄Li [14] in a similar manner as described for IV gave 0.39 g (48%, based on I) of orange-red needles; m.p. 67°C (decomp.) Found: C, 60.88; H, 5.80; O, 15.59; Fe, 17.56. C₁₆H₁₈O₃Fe (314.17) calcd.: C, 61.17; H, 5.78; O, 15.28; Fe, 17.78%. Mol. wt. 314 (mass spec.).

6. C₄H₆(CO)₂FeC(OC₂H₅)C₆H₄OCH₃-*p* (VII)

n-C₄H₉Li [15] (2.6 mmol) was mixed with a solution of 0.48 g (2.6 mmol) of *p*-CH₃OC₆H₄Br in 20 ml of ether. The mixture was stirred at room temperature for 0.5 h. The resulting solution of *p*-CH₃OC₆H₄Li [6] was added dropwise to a solution of 0.5 g (2.6 mmol) of I in 60 ml of ether at -50°C within 20 min. Subsequent treatment in a similar manner as described in 2 gave orange-red crystals. m.p. 68°C (decomp.) yield 0.26 g (31%, based on I) Found: C, 58.32; H, 5.48; O, 19.05; Fe, 16.64. C₁₆H₁₈O₄Fe (330.17) calcd.: C, 58.21; H, 5.50; O, 19.38; Fe, 16.91%. Mol. wt. 330 (mass spec.).

7. C₄H₆(CO)₂FeC(OC₂H₅)C₆H₄Cl-*p* (VIII)

n-C₄H₉Li (4.3 mmol) was mixed with a solution of 0.55 g (2.9 mmol) of *p*-ClC₆H₄Br in 20 ml of ether at 0°C. After stirring at room temperature for 20 min, the resulting solution of *p*-ClC₆H₄Li [16] was added dropwise to a solution of 0.5 g (2.6 mmol) of I in 60 ml of ether at -50°C. Subsequent treatment in a similar manner as described in 2 gave 0.38 g (44%, based on I) of orange needles. m.p. 63°C (decomp.) Found: C, 53.92; H, 4.62; Cl, 10.74; Fe, 16.80. C₁₅H₁₅O₃ClFe (334.59) calcd.: C, 53.85; H, 4.52; Cl, 10.60; Fe, 16.69%. Mol. wt. 334 (mass spec.).

8. C₄H₆(CO)₂FeC(OC₂H₅)C₆H₄Cl-*m* (IX)

To a solution (-40°C) of 3.8 mmol of *n*-C₄H₉Li in 20 ml of ether, cooled to -40°C, was added dropwise 0.73 g (3.8 mmol) of *m*-ClC₆H₄Br in 15 ml of ether within 3 min. After 9 min stirring at -35°C, the resulting solution of *m*-ClC₆H₄Li [17] reacted with I in a similar manner as described in 3 to give 0.34 g (39%, based on I) of orange needles. m.p. 62°C (decomp.). Found: C, 54.06; H, 4.64; Cl, 10.64; Fe, 16.92. C₁₅H₁₅O₃ClFe (334.59) calcd.: C, 53.85; H, 4.52; Cl, 10.60; Fe, 16.69%. Mol. wt. 334 (mass spec.).

9. C₄H₆(CO)₂FeC(OC₂H₅)C₆H₄CF₃-*p* (X)

A solution of 5.2 mmol of *n*-C₄H₉Li in 20 ml of ether was added dropwise to a solution of 1.16 g (5.2 mmol) of *p*-CF₃C₆H₄Br in 20 ml ether. After 20 min stirring at room temperature the resulting solution of *p*-CF₃C₆H₄Li [18] was reacted, in a manner similar to that described in 3, with 1.0 g (5.2 mmol) of I in 50 ml of ether at -50°C to give 1.23 g (65%, based on I) of orange-red needles, m.p. 73°C (decomp.) Found: C, 52.39; H, 4.34; F, 15.60; Fe, 15.35. C₁₆H₁₅O₃F₃Fe (368.14) calcd.: C, 52.20; H, 4.11; F, 15.49; Fe, 15.17%. Mol. wt. 368 (mass spec.).

10. $C_4H_6(CO)_2FeC(OC_2H_5)C_{10}H_7-\alpha$ (XI)

The reaction of 1.0 g (5.2 mmol) of I in 50 ml of ether with 5.2 mmol of $\alpha-C_{10}H_7Li$ [13] at $-50^\circ C$, in a similar manner as described for IV, gave 0.17 g (9.4%, based on I) of orange crystals. m.p. $101^\circ C$ (decomp.) Found: C, 64.99; H, 5.44; O, 13.91; Fe, 15.81. $C_{19}H_{18}O_3Fe$ (350.20) calcd.: C, 65.17; H, 5.18; O, 13.71; Fe, 15.95%. Mol. wt. 350 (mass spec.).

11. $C_4H_6(CO)_2FeC(OC_2H_5)C_4H_3S-2$ (XII)

To a solution of 0.305 g (3.6 mmol) of thiophene in 100 ml of ether was added 3.3 mmol of $n-C_4H_9Li$. After 20 min stirring, the resulting solution of $2-C_4H_3SLi$ [19] reacted with 0.5 g (2.6 mmol) of I at $-50^\circ C$, similarly as described in 3, to give orange-red crystals. m.p. $45^\circ C$ (decomp.), yield 0.21 g (27%, based on I). Found: C, 50.70; H, 4.45; O, 15.31; S, 10.44; Fe, 18.39. $C_{13}H_{14}O_3SFe$ (306.16) calcd.: C, 51.00; H, 4.61; O, 15.68; S, 10.47; Fe, 18.24%. Mol. wt. 306 (mass spec.).

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