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ASYMMETRIC INDUCTION IN THE SYNTHESIS OF METALLOCENYLPYRAZOLINES

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Summary

The asymmetric induction in the synthesis of pyrazolines with ferrocenyl and phenylbutadienyliron tricarbonyl substituents is estimated. Diastereomeric selectivity is shown to be sufficiently high both by the induction of a chiral centre by a chirality plane and vice versa. The molecular geometry of diastereomeric 1-acetyl-3-[4-phenylbutadienyliron tricarbonyl]-5-ferrocenylpyrazolines is discussed.

Depending on the nature of chiral elements, nine variants of asymmetric induction are possible [1]. Our recent synthesis of isomeric polyenones with metallocenyl substituents [2] and isomeric pyrazolines with a phenylbutadienyl substituent [3]

SCHEME 1

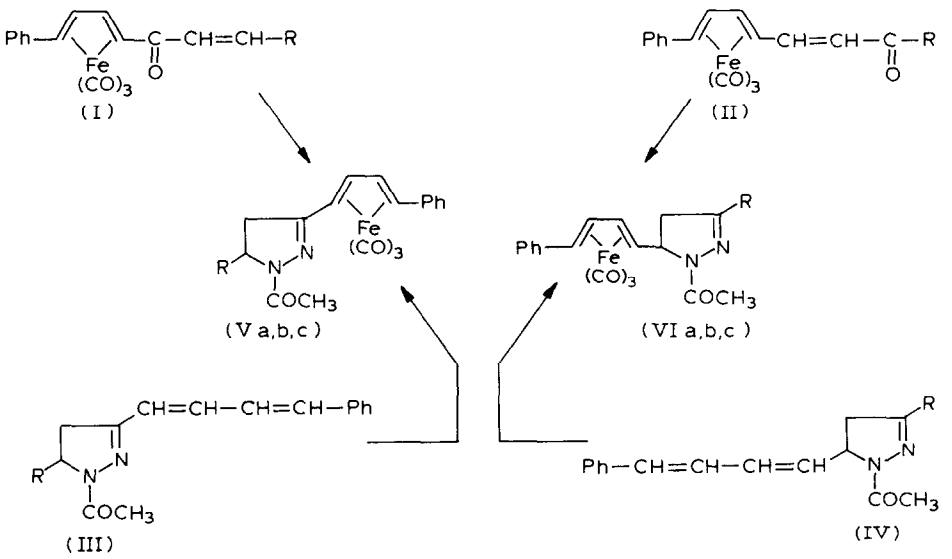

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TABLE 1
THE DEGREE OF ASYMMETRIC INDUCTION IN THE SYNTHESIS OF FERROCENYLPYRAZOLINES

Induction path	Induction variant	Induction type	Yield (%) of diastereomers		Diastereomeric selectivity(%)
			A	B	
I → V	plane → centre	1 3	58	31	27
III → V	centre → plane	1.3	52	22	30
II → VI	plane → centre	1 1	78	1	77
IV → VI	centre → plane	1.1	84	1	83

provides an opportunity to discuss asymmetric induction for two combinations, namely, chiral centre → chirality plane and chirality plane → chiral centre.

Starting from isomeric unsaturated ketones of types I and II and isomeric pyrazolines III and IV we have obtained diastereomeric (A and B) pyrazolines V and VI (*N*-acetyl derivatives) with planar and central chirality (Scheme 1).

As can be seen from Scheme 1, the 1,3-asymmetric induction is observed in the cases I → V and III → V, with the chirality plane and the chiral centre sufficiently separated. The cases II → VI and IV → VI may be considered as 1,1-asymmetric induction with the chirality plane and the chiral centre being close to each other.

Pyrazolines V and VI differ in the isomeric positions of the phenylbutadienyliron tricarbonyl substituent, which allows one to compare directly the degree of asymmetric induction, i.e. the diastereomeric selectivity (see Table 1 for ferrocenyl derivatives).

As can be seen from Table 1, the proximity or remoteness of chiral elements affects the diastereomeric selectivity *.

Data from elemental analysis of pyrazolines V and VI and their physico-chemical characteristics are given in Tables 2 and 3.

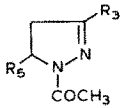
According to these tables most of properties of the isomeric pairs are similar and, as a rule, only slightly exceed experimental errors. However, isomers have different R_f values (which has been used in their separation) and melting points as is to be expected for diastereomers. It should be also noted that isomeric ferrocenyl-substituted pyrazolines VA and VB have different fluorescence spectra, which is possibly due to the more pronounced difference between diastereomers in the excited state than in the ground state.

In order to establish the structures of A and B isomers unambiguously we have carried out an X-ray diffraction study of diastereomeric 1-acetyl-3-[4-phenylbutadienyliron tricarbonyl]-5-ferrocenylpyrazolines V. Crystals of VA and VB are triclinic, at 20°C $a = 7.948(4)$ (A), 9.888(3) (B); $b = 12.960(8)$, 10.850(4); $c =$

(Continued on p. 210)

* Compounds of the cymantrene series decompose under the reaction conditions which causes the decrease of the total yield and, possibly, the loss of the second diastereomer. Thus, the 100% diastereomeric selectivity is a rather arbitrary value, though only single diastereomers have been isolated.

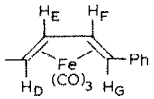
TABLE 2
YIELDS AND ANALYTICAL DATA FOR THE PYRAZOLINES V AND VI

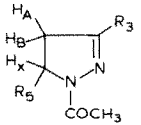


Compound	R_3	R_5	Method of synthesis	M.p. (°C)	Yield (%)	Found (calcd.) (%)				Formula
						C	H	Fe	Mn	
VIA	Fc [a]	PBIT [a]	I	206-207	78	59.42	4.08	20.01	–	
VIA	Fc	PBIT	II	206-207	84	(59.61)	(4.29)	(19.80)		
VIB	Fc	PBIT	I	186-188	1 [b]					
VIB	Fc	PBIT	II	186-188	1					
VA	PBIT	Fc	I	201-202	58	59.27	4.37	19.77	–	$C_{28}H_{24}FeN_2O_4$
VA	PBIT	Fc	II	201-202	52	(59.61)	(4.29)	(19.80)		
VB	PBIP	Fc	I	214-215	31	59.21	4.25	19.94	–	
VB	PBIP	Fc	II	214-215	22	(59.61)	(4.29)	(19.80)		
VIC	CTM [a]	PBIT	I	193-194	68	50.64	3.40	10.34	10.15	
						(50.58)	(3.51)	(10.22)	(10.06)	
VC	PBIT	CTM	I	187-188	71	50.41	3.40	10.32	10.13	$C_{26}H_{19}FeMnN_2O_7$
						(50.58)	(3.51)	(10.22)	(10.06)	

[a] Fc = $C_5H_5FeC_5H_4$, PBIT = $C_6H_5(CH{=}CH)_2Fe(CO)_3$, CTM = $C_5H_4Mn(CO)_3$. [b] Yield not determined further due to negligibility.

TABLE 3
SPECTRAL DATA FOR THE PYRAZOLINES V AND VI





Compound	R_3	R_5	R_3 ν(CO) (cm^{-1})			R_5 ν(CO) (cm^{-1})			λ_{max}, lgε				$COCH_3$ δ(ppm)
VIA	Fc	PBIT		–		2050	1987	1978	228	264	299	440	2.32
									5.10	4.92	4.87	2.80	
VA	PBIT	Fc	2058	1995			–		272	328	400	456	2.16
									4.37	4.18	3.39	2.43	
VB	PBIT	Fc	2058	1997	1992		–		276	310–336	396	456	2.15
									4.41	4.24	3.38	2.43	
VIC	CTM	PBIT	2034	1960	1945	2053	1992	1979	286	360	390		2.33
									4.53	3.65	3.25		
VC	PBIT	CTM	2059	1996		2031	1953	1944	274	306–310	410		2.23
									4.33	4.22	3.27		

Fc/CTM δ(ppm)		PBIT, δ(ppm) J(Hz)													
		C_6H_5	H_D	H_E	H_F	H_G	J_{DE}	J_{EF}	J_{FG}	H_X	H_A	H_B	J_{AX}	J_{BX}	J_{AB}
4.70 (α,1H)	4.62 (α,1H)	7.20	1.24	6.01	5.81	2.13	8.0	5.5	9.0	4.35	3.04	3.52	3.78	11.22	−17.0
4.43 (β,2H)	4.24 (γ,5H)														
4.48 (α,1H)	4.14(β + γ,7H)	7.29	1.72	6.11	5.99	2.42	8.3	5.5	8.8	5.33	3.16	3.38	3.97	11.28	−17.7
4.02 (α,1H)															
4.52 (α,1H)	4.14(β + γ,7H)	7.28	1.73	6.05	5.96	2.42	7.5	5.5	8.3	5.33	3.23	3.37	3.87	12.13	−17.0
4.00 (α,1H)															
5.31 (α,2H)	4.93 (β,2H)	7.24	1.28	6.02	5.85	2.21	8.0	5.5	9.0	4.44	2.93	3.48	3.84	11.16	−17.0
5.11 (α,1H)	4.79 (α,1H)	7.28	1.64	6.11	6.00	2.40	8.0	5.5	9.0	5.27	2.76	3.38	3.85	11.15	−18.0
4.72 (β,1H)	4.64 (β,1H)														

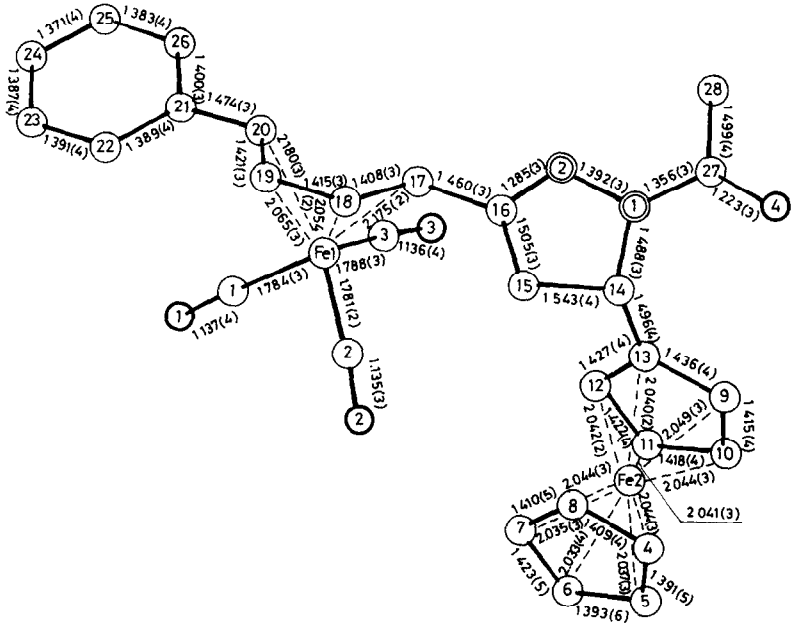


Fig. 1. Geometry of complex A.

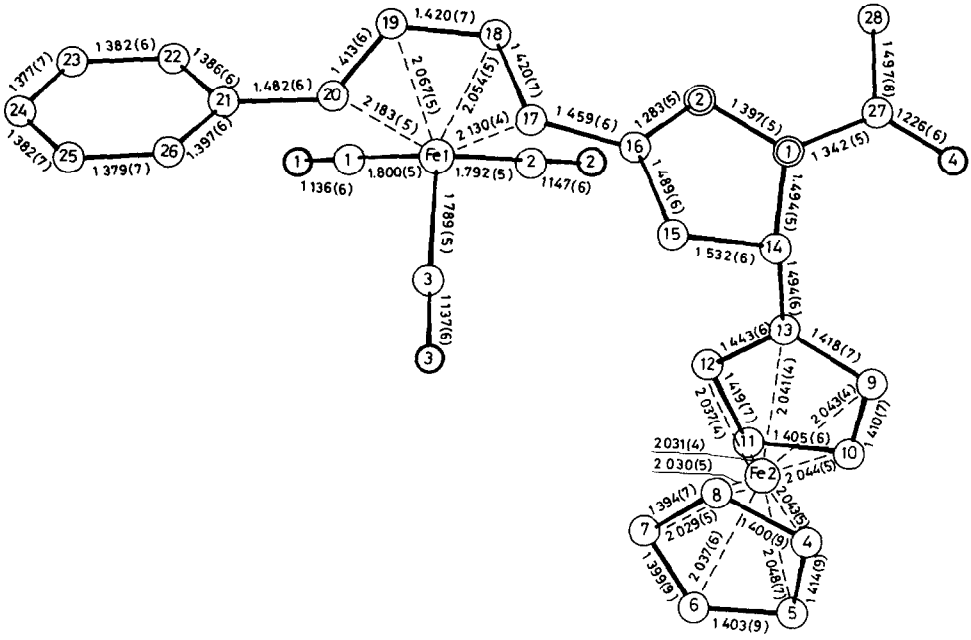


Fig. 2. Geometry of complex B.

TABLE 4

ATOMIC COORDINATES ($\times 10^4$, for Fe $\times 10^5$) AND PARAMETERS OF ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{\star 2} + \ldots + 2B_{23}klb^{\star}c^{\star})]$ in A

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	24430(4)	108222(2)	132864(2)	2.40(2)	2.64(1)	2.34(1)	1 16(1)	0 95(1)	0.88(1)
Fe(2)	30441(4)	74734(3)	92213(2)	2.44(2)	3.30(2)	2.31(2)	1.11(1)	0.64(1)	0.95(1)
O(1)	3777(3)	13184(2)	13609(2)	7.8(1)	3.13(8)	8 4(1)	1.50(9)	4.2(1)	1.98(9)
O(2)	2044(3)	10539(2)	10967(2)	6.5(1)	5.8(1)	3.01(8)	1.65(9)	2.16(8)	1.37(7)
O(3)	5943(3)	10446(2)	14116(2)	3.56(9)	9.6(2)	7.0(1)	3.6(1)	1.84(9)	4.3(1)
O(4)	2209(3)	4900(1)	11511(2)	6.0(1)	2.78(7)	5.00(9)	1.58(7)	1.78(8)	1.01(7)
N(1)	1920(3)	6592(2)	12108(2)	4.7(1)	2.69(7)	3.09(8)	1.52(7)	1.67(8)	1.09(6)
N(2)	2034(3)	7495(1)	12960(2)	3.84(9)	2.80(7)	2.93(8)	1.14(7)	1.48(7)	0.97(6)
C(1)	3207(4)	12267(2)	13477(2)	4.2(1)	3.5(1)	3.8(1)	1.72(9)	1.93(9)	1.23(8)
C(2)	2212(3)	10609(2)	11865(2)	3.4(1)	3.47(9)	3.15(9)	1.29(8)	1.57(8)	1.09(8)
C(3)	4589(4)	10614(2)	13829(2)	3.4(1)	4.4(1)	3.7(1)	1 65(9)	1 48(9)	1 81(9)
C(4)	1133(4)	6789(3)	7730(2)	4.4(1)	5.2(1)	3.0(1)	1.7(1)	−0.02(9)	0.52(9)
C(5)	2706(5)	7391(3)	7614(2)	5.2(2)	9.2(2)	3.3(1)	4.1(2)	2.1(1)	2.7(1)
C(6)	3104(4)	8482(3)	8242(3)	3.8(1)	7.1(2)	5.7(2)	0.9(1)	0.7(1)	4.4(2)
C(7)	1736(5)	8564(2)	8763(2)	6.0(2)	4.7(1)	3.4(1)	3.0(1)	0.3(1)	1.41(9)
C(8)	516(4)	7506(2)	8441(2)	3.3(1)	5.8(1)	3.5(1)	2.1(1)	0 9(1)	1.9(1)
C(9)	3456(3)	6225(2)	9879(2)	4.0(1)	3.49(9)	2.74(9)	1.76(8)	1.01(8)	0.95(8)

C(10)	5054(4)	6770(2)	9706(2)	3.8(1)	5.4(1)	3.5(1)	2.6(1)	1.36(9)	1.80(9)
C(11)	5542(3)	7895(2)	10322(2)	2.6(1)	5.5(1)	3.6(1)	0.81(9)	0.41(9)	1.9(1)
C(12)	4235(3)	8049(2)	10876(2)	3.4(1)	3.40(9)	2.67(9)	0.78(8)	0.44(8)	0.81(7)
C(13)	2914(3)	7019(2)	10596(2)	3.1(1)	2.83(9)	2.45(8)	1.15(7)	0.75(7)	0.86(7)
C(14)	1325(3)	6770(2)	11014(2)	3.3(1)	2.58(8)	2.88(9)	0.92(7)	0.95(8)	0.72(7)
C(15)	530(3)	7749(2)	11310(2)	3.5(1)	3.36(9)	2.83(9)	1.48(8)	1.07(8)	0.73(7)
C(16)	1292(3)	8154(2)	12538(2)	2.87(9)	2.75(8)	2.79(9)	0.92(7)	1.17(7)	0.85(7)
C(17)	1200(3)	9157(2)	13276(2)	3.05(9)	2.76(8)	2.63(8)	0.94(7)	1.16(7)	0.81(7)
C(18)	−39(3)	9749(2)	12974(2)	2.41(9)	3.36(9)	2.74(8)	0.84(7)	0.95(7)	0.79(7)
C(19)	98(3)	10763(2)	13720(2)	2.63(9)	3.52(9)	2.79(9)	1.34(8)	1.11(8)	0.87(7)
C(20)	1502(3)	11145(2)	14728(2)	2.91(9)	3.23(9)	2.65(8)	1.43(7)	1.33(8)	1.08(7)
C(21)	1863(3)	12239(2)	15510(2)	2.96(9)	3.45(9)	2.54(8)	1.35(8)	1.29(7)	0.81(7)
C(22)	1243(4)	13090(2)	15222(2)	4.9(1)	4.5(1)	2.81(9)	2.7(1)	0.97(9)	0.80(9)
C(23)	1607(5)	14096(2)	15990(2)	6.2(2)	4.5(1)	3.9(1)	3.2(1)	1.3(1)	0.6(1)
C(24)	2580(4)	14263(2)	17069(2)	5.6(2)	4.4(1)	3.5(1)	2.1(1)	1.2(1)	−0.30(9)
C(25)	3187(4)	13430(2)	17371(2)	4.3(1)	4.9(1)	2.57(9)	1.2(1)	0.70(9)	0.38(9)
C(26)	2857(3)	12428(2)	16601(2)	3.3(1)	3.8(1)	2.73(9)	1.15(8)	0.92(8)	1.01(8)
C(27)	2358(3)	5679(2)	12288(2)	3.9(1)	2.83(9)	4.6(1)	1.19(8)	1.80(9)	1.55(9)
C(28)	3001(6)	5690(3)	13461(3)	5.6(2)	3.8(1)	4.7(1)	1.9(1)	1.7(1)	2.2(1)

TABLE 5

ATOMIC COORDINATES ($\times 10^4$, for Fe $\times 10^5$) AND PARAMETERS OF ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)]$ in B

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	3815(6)	29041(5)	11767(4)	2.45(3)	2.68(3)	3.54(3)	0.99(2)	1.48(2)	1.04(2)
Fe(2)	−37552(6)	22552(5)	40818(4)	2.80(3)	2.38(3)	3.73(3)	1.01(2)	1 63(2)	0.55(5)
O(1)	−597(4)	3158(4)	1016(3)	5.5(2)	10.2(3)	4.6(2)	2.4(2)	1.7(2)	3.6(2)
O(2)	−2409(4)	329(3)	438(3)	5.6(2)	4.2(2)	7.6(2)	−1.2(2)	1.4(2)	0.7(2)
O(3)	−483(4)	4836(3)	2325(3)	6.0(2)	5.2(2)	5.1(2)	3.5(2)	2.0(1)	0.6(1)
O(4)	−2519(4)	−1831(3)	4028(3)	5.4(2)	3.8(1)	5.3(2)	1.9(1)	3.1(1)	2 4(1)
N(1)	−1148(4)	−153(3)	3432(3)	3.7(2)	2.6(1)	4.1(2)	1.6(1)	2.2(1)	1 4(1)
N(2)	−215(4)	336(3)	2828(3)	3.7(2)	4.0(2)	4.1(2)	2.2(1)	2 5(1)	1.8(1)
C(1)	−181(5)	3091(4)	−162(4)	3.1(2)	4.8(2)	4.8(2)	1.2(2)	2.0(2)	1.9(2)
C(2)	−1320(6)	1326(5)	748(4)	4.4(2)	3.6(2)	4.4(2)	1.2(2)	1.9(2)	1.3(2)
C(3)	−146(5)	4105(4)	1848(3)	2.8(2)	3.7(2)	3.9(2)	1.2(2)	1.1(2)	1.5(2)
C(4)	−3173(7)	3163(5)	5663(4)	7.9(4)	4.6(2)	4.7(2)	2.4(2)	3.4(3)	0 3(2)
C(5)	−4523(7)	3253(5)	5057(5)	5.5(3)	3.9(2)	9 3(4)	1.2(2)	4.7(3)	−0.8(2)
C(6)	−4156(7)	3969(5)	4303(5)	5.9(3)	3.8(2)	8.2(3)	2.8(2)	2.0(3)	0 4(2)
C(7)	−2598(6)	4324(4)	4437(4)	5.9(3)	2.8(2)	6.2(3)	1 1(2)	2 8(2)	0.9(2)

C(8)	−1999(5)	3835(5)	5274(4)	3.9(2)	3.8(2)	4.8(2)	1.0(2)	1.2(2)	−0.9(2)
C(9)	−4223(5)	225(4)	3905(3)	3.6(2)	2.5(2)	4.4(2)	1.0(1)	2.1(2)	0.6(1)
C(10)	−5497(5)	371(4)	3249(4)	2.6(2)	3.1(2)	5.6(2)	0.7(2)	1.4(2)	−0.0(2)
C(11)	−5004(5)	1132(4)	2547(3)	3.6(2)	4.1(2)	4.0(2)	1.7(2)	0.7(2)	0.3(2)
C(12)	−3412(5)	1463(4)	2752(3)	3.3(2)	3.7(2)	3.4(2)	2.0(2)	1.3(2)	0.5(2)
C(13)	−2917(4)	896(4)	3614(3)	2.8(2)	2.4(2)	3.2(2)	0.9(1)	1.3(1)	0.3(1)
C(14)	−1335(4)	966(4)	4086(3)	3.3(2)	2.4(2)	3.1(2)	1.2(1)	1.5(1)	1.3(1)
C(15)	−24(5)	2222(4)	4024(3)	2.8(2)	2.8(2)	4.0(2)	1.0(1)	1.3(2)	0.9(1)
C(16)	389(4)	1650(4)	3134(3)	2.8(2)	3.3(2)	3.9(2)	1.6(2)	1.5(2)	1.6(2)
C(17)	1381(5)	2528(4)	2647(3)	2.8(2)	3.9(2)	4.8(2)	1.7(2)	1.8(2)	2.2(2)
C(18)	1803(5)	2012(4)	1803(4)	3.2(2)	4.2(2)	5.8(2)	2.2(2)	2.4(2)	2.2(2)
C(19)	2517(5)	2948(4)	1260(4)	3.1(2)	4.0(2)	5.1(2)	1.8(2)	2.4(2)	1.8(2)
C(20)	2795(4)	4337(4)	1603(3)	2.4(2)	4.0(2)	4.3(2)	1.3(1)	1.6(2)	1.6(2)
C(21)	3369(4)	5377(4)	1029(3)	2.3(2)	3.8(2)	3.6(2)	1.1(1)	1.4(1)	1.1(2)
C(22)	3239(5)	5057(4)	−37(3)	3.5(2)	3.3(2)	3.7(2)	0.4(2)	1.4(2)	0.7(2)
C(23)	3817(5)	6068(5)	−529(3)	3.4(2)	4.9(2)	3.8(2)	1.0(2)	1.5(2)	1.4(2)
C(24)	4538(5)	7428(5)	33(4)	3.7(2)	4.0(2)	5.8(3)	0.9(2)	2.1(2)	2.1(2)
C(25)	4679(6)	7772(5)	1097(4)	5.9(3)	3.2(2)	5.7(3)	0.5(2)	2.6(2)	0.5(2)
C(26)	4109(5)	6762(4)	1588(3)	4.7(2)	3.5(2)	3.9(2)	0.5(2)	2.2(2)	0.8(2)
C(27)	−1774(5)	−1476(4)	3439(3)	4.1(2)	2.9(2)	4.2(2)	1.8(2)	1.4(2)	1.1(2)
C(28)	−1495(7)	−2460(4)	2710(4)	8.5(4)	3.1(2)	7.1(3)	2.8(2)	4.2(3)	1.3(2)

TABLE 6

BOND ANGLES ω (°) IN STRUCTURE A

Angle	ω	Angle	ω	Angle	ω
C(1)Fe(1)C(2)	88.2(1)	C(10)C(9)C(13)	108.5(2)	C(17)C(18)C(19)	118.4(2)
C(1)Fe(1)C(3)	97.4(1)	C(9)C(10)C(11)	108.1(2)	C(18)C(19)C(20)	118.3(2)
C(2)Fe(1)C(3)	104.0(1)	C(10)C(11)C(12)	108.1(2)	C(19)C(20)C(21)	122.3(2)
N(2)N(1)C(14)	112.4(2)	C(11)C(12)C(13)	108.4(2)	C(20)C(21)C(22)	123.2(2)
N(2)N(1)C(27)	122.2(2)	C(9)C(13)C(12)	106.9(2)	C(20)C(21)C(26)	118.6(2)
C(14)N(1)C(27)	125.3(2)	C(9)C(13)C(14)	125.4(2)	C(22)C(21)C(26)	118.2(2)
N(1)N(2)C(16)	107.9(2)	C(12)C(13)C(14)	127.6(2)	C(21)C(22)C(23)	120.9(3)
Fe(1)C(1)O(1)	176.7(3)	N(1)C(14)C(13)	109.3(2)	C(22)C(23)C(24)	120.1(3)
Fe(1)C(2)O(2)	175.5(2)	N(1)C(14)C(15)	100.3(2)	C(23)C(24)C(25)	119.9(3)
Fe(1)C(3)O(3)	176.1(3)	C(13)C(14)C(15)	114.6(2)	C(24)C(25)C(26)	120.2(3)
C(5)C(4)C(8)	108.4(3)	C(14)C(15)C(16)	102.2(2)	C(21)C(26)C(25)	120.8(2)
C(4)C(5)C(6)	108.9(3)	N(2)C(16)C(15)	114.1(2)	O(4)C(27)N(1)	119.8(2)
C(5)C(6)C(7)	107.6(3)	N(2)C(16)C(17)	118.3(2)	O(4)C(27)C(28)	123.6(3)
C(6)C(7)C(8)	107.6(3)	C(15)C(16)C(17)	127.5(2)	N(1)C(27)C(28)	116.6(3)
C(4)C(8)C(7)	107.5(3)	C(16)C(17)C(18)	123.3(2)		

13.126(10),13.437(4) Å; α = 103.19(6), 98.02(3); β = 103.62(5),105.25(2); γ = 101.95(5), 111.38(3)°; V = 1250; 1230 Å^3; M = 564.2; d_{calcd} = 1.52, 1.50 g/cm^3 for Z = 2; space group $P\bar{1}$; $\mu(\lambda\text{Mo-}K_\alpha)$ = 12.4 cm^{-1}. Intensities of 4065 (A) and 2594 (B) reflections with $I \geq 2\sigma$ were measured with an automatic diffractometer Syntex $P2_1$(λMo-K_α, graphite monochromator, $\theta/2\theta$ scan) neglecting absorption corrections. Both structures were solved by the direct method with the MULTAN program and refined by the full-matrix anisotropic least squares. All H atoms found in difference syntheses were included in refinement with fixed positional and temperature parameters (B_{iso} = 5.5 (A), 6.0 (B) Å^2). The final discrepancy factors are R = 0.037 (A), 0.040 (B); R_w = 0.053,0.054. Coordinates of non-hydrogen atoms and

TABLE 7

BOND ANGLES ω (°) IN STRUCTURE B

Angle	ω	Angle	ω	Angle	ω
C(1)Fe(1)C(2)	88.1(2)	C(10)C(9)C(13)	108.7(4)	C(17)C(18)C(19)	117.6(4)
C(1)Fe(1)C(3)	100.4(2)	C(9)C(10)C(11)	108.3(4)	C(18)C(19)C(20)	118.4(4)
C(2)Fe(1)C(3)	103.7(2)	C(10)C(11)C(12)	108.7(4)	C(19)C(20)C(21)	123.4(4)
N(2)N(1)C(14)	112.3(3)	C(11)C(12)C(13)	107.3(4)	C(20)C(21)C(22)	123.8(4)
N(2)N(1)C(27)	123.5(4)	C(9)C(13)C(12)	107.1(4)	C(20)C(21)C(26)	118.8(4)
C(14)N(1)C(27)	124.1(4)	C(9)C(13)C(14)	126.5(4)	C(22)C(21)C(26)	117.4(4)
N(1)N(2)C(16)	107.5(4)	C(12)C(13)C(14)	126.3(4)	C(21)C(22)C(23)	121.4(7)
Fe(1)C(1)O(1)	176.9(5)	N(1)C(14)C(13)	110.3(3)	C(22)C(23)C(24)	120.4(5)
Fe(1)C(2)O(2)	177.4(5)	N(1)C(14)C(15)	100.1(3)	C(23)C(24)C(25)	119 2(5)
Fe(1)C(3)O(3)	176.0(4)	C(13)C(14)C(15)	114.9(3)	C(24)C(25)C(26)	120.3(5)
C(5)C(4)C(8)	107.2(5)	C(14)C(15)C(16)	103.0(3)	C(21)C(26)C(25)	121.3(5)
C(4)C(5)C(6)	107.7(6)	N(2)C(16)C(15)	114.5(4)	O(4)C(27)N(1)	120.4(4)
C(5)C(6)C(7)	108.3(5)	N(2)C(16)C(17)	123.4(4)	O(4)C(27)C(28)	122.9(4)
C(6)C(7)C(8)	107 7(5)	C(15)C(16)C(17)	122.1(4)	N(1)C(27)C(28)	116.7(4)
C(4)C(8)C(7)	109.0(5)	C(16)C(17)C(18)	123.3(4)		

their temperature factors are given in Tables 4 and 5, bond angles in Tables 6 and 7, bond lengths are shown in Figs. 1 and 2.

The results show that the molecules A and B are, in fact, geometric isomers with different orientations of the phenylbutadienyliron tricarbonyl substituents as is seen from the values of the torsion angles around the C(pyrazoline)–C(butadiene) bond: while in A the angles C(18)C(17)C(16)N(2) and C(18)C(17)C(16)C(15) are −158.3(3) and 18.0(2)° respectively (*trans* configuration of the double bonds C(17)=C(18) and C(16)=N(2)); in B these angles are −1.5(4) and 179.5(5)°, (*cis* configuration).

It is essential that both molecules have the cisoid conformation with respect to arrangement of the organometallic fragments, viz. the iron tricarbonyl fragment and the ferrocenyl substituent are situated on one side of the plane of the pyrazoline ring. It is obvious that the transition from the *trans* to the *cis* configuration by rotation of the phenylbutadienyl substituent around the C(16)–C(17) bond by 180° changes the sign of planar chirality of the phenylbutadienyliron tricarbonyl fragment in accordance with the diastereomeric correlation between molecules A and B.

Bond lengths and angles in molecules A and B are fairly close. The pyrazoline rings in A and B are non-planar but folded along the line N(1) ··· C(15) by 16.8° (A) and 15.2° (B) thus acquiring an envelope-like conformation (Table 8) with ferrocenyl groups in the pseudoaxial positions due to obvious steric reasons (close proximity to the acetyl substituent in the pseudoequatorial orientation). At the same time, the substituted Cp rings are almost perpendicular to the planar fragments N(1)–N(2)–C(16)–C(15) of the pyrazoline rings with corresponding dihedral angles $\tau = 93.6°$ (A) and 83.5° (B). On the other hand, the rotation of acetyl ($\tau = 9.5°$ (A) and 10.1° (B)) and butadienyl ($\tau = 23.7°$ (A) and 13.8° (B)) substituents relative to the above-mentioned planar fragment N(1)–N(2)–C(16)–C(15) is rather small, so that conjugation of these parts of molecules A and B with possible participation of the phenyl substituent (Table 8) is retained. A noticeable difference in the angles of rotation of butadiene fragments in A and B is evidently due to the less favourable *trans* configuration of the C(18)=C(17) and C(16)=N(2) bonds in A, which gives rise to shortened intramolecular contacts between the H atoms at C(18) and C(15).

In the pyrazoline rings of A and B the bonds N(2)=C(16) are somewhat elongated and the N(1)–N(2) bonds, on the contrary, shortened in comparison with the standard lengths of C=N (1.23 Å [4]) and N–N (1.45 Å [5]) bonds, whereas other bond lengths are close to the expected values. Shortening of the exocyclic peptide N(1)–C(27) bonds to 1.356(3) (A) and 1.342(5) Å (B) should be also noted.

As in numerous other complexes of the (diene)$Fe(CO)_3$ type, the coordination polyhedron of the Fe(1) atom in A and B is a tetragonal pyramid with one of the carbonyl groups in the apical position in this case (C(3)–O(3)). In such a description of coordination the non-equivalence of π-interactions of the metal with the carbonyl groups is assumed. This follows from the symmetry of non-bonding orbitals of a metal atom and leads to the non-equivalence of carbonyl ligands in (diene)$Fe(CO)_3$ complexes. The latter effect is confirmed by numerous IR spectroscopic studies (e.g. [6]) and by X-ray diffraction data showing noticeable disturbance of the C_{3v} symmetry of a $Fe(CO)_3$ fragment where two bond angles (O)C–Fe–C(O) involving an apical CO group are considerably larger than the third angle. The same situation is observed in complexes A and B (see Tables 6 and 7).

Structural studies of π-butadiene complexes of transition metals show [7], that the distribution of bond lengths in the butadiene ligand is strongly dependent on the

TABLE 8

DEVIATIONS (Δ, Å) OF ATOMS FROM THE MEAN PLANES

Plane 1	Δ		Plane 4	Δ	
	A	B		A	B
C(4)	0.000(3)	0.003(5)	C(17)	−0.003(2)	0 003(5)
C(5)	0.000(3)	−0.002(6)	C(18)	0.005(2)	−0 006(5)
C(6)	−0 001(4)	−0.001(6)	C(19)	−0.005(2)	0 006(5)
C(7)	0.001(3)	0.002(5)	C(20)	0.003(2)	−0.003(5)
C(8)	−0.000(3)	−0.003(5)	C(16) [a]	0.126(2)	0 246(4)
			C(21) [a]	0.123(2)	0 160(4)
Plane 2	Δ		Plane 5	Δ	
	A	B		A	B
C(9)	−0.007(2)	0.001(4)	C(21)	−0.001(2)	0.001(5)
C(10)	0.005(3)	0.002(5)	C(22)	−0.005(3)	0.000(5)
C(11)	0.002(3)	−0.003(4)	C(23)	0 007(4)	−0.001(5)
C(12)	−0.006(2)	0.003(4)	C(24)	0 002(4)	0.000(6)
C(13)	0.006(2)	−0.002(4)	C(25)	−0.008(3)	0.002(6)
			C(26)	0.007(3)	−0.002(6)
			C(20) [a]	−0.025(2)	−0.018(5)
Plane 3	Δ		Plane 6	Δ	
	A	B		A	B
N(1)	0.003(2)	0.004(4)	N(1)	0.000(2)	−0.001(4)
N(2)	−0.005(2)	−0.009(4)	C(27)	−0.002(3)	0.004(5)
C(16)	0.006(2)	0.012(4)	C(28)	0 001(5)	−0.002(6)
C(15)	−0.004(3)	−0.006(4)	O(4)	0.000(2)	−0.001(4)
Fe(1) [a]	1.5119(3)	1.9297(6)			
Fe(2) [a]	2.7354(3)	2.5904(6)			
C(14) [a]	0 280(3)	0.254(4)			
C(17) [a]	−0.035(2)	0 070(5)			
C(27) [a]	−0.190(3)	−0.212(5)			

COEFFICIENTS OF PLANE EQUATIONS ($AX + BY + CZ - D = 0$) IN ORTHOGONAL COORDINATE SYSTEM

Plane	A		B		C		D	
	A	B	A	B	A	B	A	B
1	−0.4244	0.2483	0.4567	−0.7158	−0 7819	−0.6527	−3.3514	−7.1253
2	−0.4218	0.2635	0.4533	−0.6985	−0.7852	−0.6653	−6.7122	−3.9710
3	0.8522	−0.7097	0.5171	0.2098	−0.0794	−0.6726	−2 5775	−1.5457
4	0 6547	−0.7606	0.6266	−0.0242	−0 4228	−0.6488	−6.3340	−1.7577
5	0.8883	−0.9545	0.4075	0.1390	−0.2117	−0.2640	−5 8938	−0.4368
6	−0.9146	−0.6878	−0.4076	0.0426	−0.0240	−0 7247	1.7328	−1.5940

SOME DIHEDRAL ANGLES τ (°)

Plane	τ		Plane	τ	
	A	B		A	B
1-2	0.3	1.5	3-4	23 7	13.8
1-3	93.6	83.5	3-6	9.5	10.1
			4-5	22.1	26.6

[a] Atoms not included in mean squares plane equations.

character of the ligand in the *trans* position to the butadiene system. The effect of trans partners, defining the degree of charge transfer (dative bonding) to the butadiene ligand, in the case of strong π-acceptors (carbonyl groups) leads to more equal C–C bond lengths in the butadiene system and in the case of a weak acceptors (e.g. cyclopentadienyl) to their alternation, but in the opposite sense compared to the butadiene molecule. In the structures A and B all C–C bond lengths in the butadiene system are equal within accuracy limits (mean values 1.415(3) (A) and 1.418(7) Å (B)) and are comparable to those observed in other (diene)$Fe(CO)_3$ complexes [7]. Furthermore, in complexes of this type inequality of Fe–C(butadiene) distances is almost always observed with mean Fe–C (terminal) values of 2.178(2) Å in A and 2.156(5) Å in B.

The ferrocene sandwiches in both molecules have an eclipsed conformation. Mean interatomic Fe–C (2.041(3) (A) and 2.037(5) Å (B)) and C–C (1.414(4) (A) and 1.410(7) Å (B)) distances are close to those found in ferrocene [8] and its derivatives. Geometrical parameters of other fragments in the molecules A and B are unexceptional.

Experimental

Synthesis of the pyrazolines was carried out by two methods. Method 1: 0.5 ml of hydrazine hydrate in 10 ml of alcohol was added to 2 mmol of the unsaturated ketone with the phenylbutadienyliron tricarbonyl substituent and the mixture was boiled for 2 h *. On cooling, the excess of hydrazine was neutralized with glacial acetic acid. Then, 5 ml of acetic anhydride was added and the reaction mixture was heated for 15 min. After cooling and neutralization with sodium carbonate, the mixture was extracted with benzene. The product was purified by chromatography on SiO_2 with a 1/1.5 mixture of petroleum ether/ether and crystallisation from aqueous alcohol.

Method 2: The mixture of 2 mmol of 1-acetyl-3,5-disubstituted pyrazoline in absolute benzene and 1.5 mmol of $Fe_3(CO)_{12}$ was boiled for 2 h under argon. On cooling, the reaction mixture was purified by chromatography on SiO_2 and crystallization from aqueous alcohol. Mixed samples obtained by both methods give no depression of the melting point.

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* Pyrazolines unsubstituted at the nitrogen atom of the cymantrene series were obtained at room temperature after 5 h.