Journal of Organometallic Chemistry, 345 (1988) 313–320
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

IR spectral and X-ray single crystal study of hydrogen bonds and structure of nonamethylferrocenyl- and ferrocenylcarbinols in the solid state

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(Received October 29th, 1987)

Abstract

The influence of different substituents in the Cp-ring and at the carbinol C atom on the character and stability of H bonds in crystals of FcCHROH and ^{9}FcCHROH, Fc = $C_5H_5FeC_5H_4$; ^{9}Fc = $C_5Me_5FeC_5Me_4$, (R = H, CH_3, C_6H_5, C_6F_5) was studied by IR spectroscopy specifically in the ν(OH) region. In these crystals, molecules associate predominantly via intermolecular OH $\cdots$ O bonds. However, in some of the ^{9}FcCHROH complexes, the intermolecular O–H $\cdots$ π(Cp) H bonds are also formed. The major type of self-association in compounds with R = Mes is OH $\cdots$ π(Mes) H-bonding. It was found from the X-ray structural data for the ^{9}FcCHMesOH that the Mes plane is almost perpendicular to each Cp ring plane. No intermolecular OH $\cdots$ O bonds are formed because of intramolecular shielding of the OH group. The stability of the intermolecular hydrogen bonds is determined by steric rather than electronic factors, the most stable intermolecular hydrogen bonds being formed in the case of primary carbinols.

In previous papers [1,2] the interesting phenomenon of carbenium ions stabilized by nonamethylferrocenyl substituents has been described. In this connection it would be quite appropriate to raise the question whether the properties of ferrocenylcarbenium ions are related to the physico-chemical characteristics of the corresponding initial carbinols.

In order to establish the effect of substituents in the Cp rings (Me) and at the carbinol C atom (R) on the character and relative stability of intermolecular hydrogen bonds in the solid state, an IR spectral study of ferrocenylcarbinols, an X-ray diffraction study and a conformational calculation were carried out on the sterically most crowded ^{9}FcCHMesOH (^{9}Fc = $C_5Me_5FeC_5Me_4$), and is described

Table 1

IR spectra of the compounds ^{9}FcCHROH, FcCHROH in the ν(OH) region in Nujol or hexachlorobutadiene, and the enthalpies ($-\Delta H$) of the intermolecular hydrogen bonds (kcal/mol)

R	^{9}FcCHROH (I)			FcCHROH (II)			
	ν(OH) (cm^{-1})	$\Delta\nu$ (cm^{-1})	$-\Delta H$	ν(OH) (cm^{-1})	$\Delta\nu$ (cm^{-1})	$-\Delta H$	Assignment
H (a)	3190br	430	6.7	3190br	430	6.7	$\nu(\mathrm{OH}\cdots\mathrm{O})$
CH_3 (b)	3555w	70	1.6	–	–	–	$\nu(\mathrm{OH}\cdots\pi(\mathrm{C}_p^\star))$
	3460m.br	160	3.3	3220v.br	317	5.6	$\nu(\mathrm{OH}\cdots\mathrm{O})$
C_6H_5 (c)	3545w	68	1.6	–	–	–	$\nu(\mathrm{OH}\cdots\pi(\mathrm{C}_p^\star))$
	3450s.br	163	3.3	3460m.br	162	3.3	$\nu(\mathrm{OH}\cdots\mathrm{O})$
C_6F_5 (d)	3550	60	1.4	–	–	–	$\nu(\mathrm{OH}\cdots\pi(\mathrm{C}_p^\star))$
	3420br	190	3.9	3350	260	4.7	$\nu(\mathrm{OH}\cdots\mathrm{O})$
Mes (e)	3550s.nar.	65	1.5	3565m.nar	55	1.3	$\nu(\mathrm{OH}\cdots\pi(\mathrm{Mes}))$
				3380w.br	230	4.4	$\nu(\mathrm{OH}\cdots\mathrm{O})$

herein. IR spectral data in the region of the ν(OH) stretching vibrations have been obtained for the following carbinols: ^{9}FcCHROH (I), FcCHROH, Fc = $C_5H_5FeC_5H_4$, (II), (R = H (a), CH_3 (b), C_6H_5 (c), C_6F_5 (d), $C_6H_2(CH_3)_3$ = Mes (e), Bu^t (f)).

As for most organic alcohols, the major type of self-association for all the carbinols investigated except for Ie and IIe is the intermolecular OH $\cdots$ O hydrogen bond. As can be seen from Table 1 the ν(OH) vibrations are broad bands in the region 3450 to 3150 cm^{-1}. An unusual type of self-association has been found in the compounds with the mesityl substituent, because of extreme steric crowding (Ie, IIe). Only the weak $\nu(\mathrm{OH}\cdots\mathrm{O})$ absorption band is observed in the spectrum of ferrocenylcarbinol (IIe); and no more than a low frequency shoulder (over 3400 cm^{-1}) of a narrow intense band 3550 cm^{-1} is observed in the spectrum of nonamethyl-substituted derivative (Ie). The position of the main absorption band in the spectrum of IIe (3565 cm^{-1}) is almost the same as that for Ie. It is well known [3,4] that the high frequency bands (> 3540 cm^{-1}) correspond to intermolecular OH $\cdots$ π H bonds, so that these bands can be assigned to vibrations of the OH group, which is H-bonded to the mesityl π-electron system. Our suggestion that the intermolecular hydrogen bonds OH $\cdots$ π(Mes) are the main way of association of the carbinols with the bulky Mes-substituent at the carbinol C atom is in good agreement with the results of an X-ray diffraction study on Ie (see below). Spectra of the secondary nonamethylferrocenylcarbinols Ib–d, show weak absorption in the $\nu(\mathrm{OH}\cdots\pi)$ region (3540–3550 cm^{-1}), along with the intense $\nu(\mathrm{OH}\cdots\mathrm{O})$ bands; the $\nu(\mathrm{OH}\cdots\mathrm{O})$ and $\nu(\mathrm{OH}\cdots\pi)$ bands being overlapped in the spectrum of Id. The similarity of the spectra of compounds Ib and Ic with R = Me and R = Ph, respectively, implies that these compounds are linked to the complexes by OH $\cdots$ π(Cp*) * interaction. No self-association by OH $\cdots$ π(Cp) bonding is observed in the analogous ferrocenylcarbinols IIb, IIc. The electron-donating effect of nine Me groups apparently overrules the steric factors, which make the formation of intermolecular hydrogen bonds involving the Cp*-rings unfavourable.

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* Cp = C_5H_5; Cp* = C_5Me_5.

The values of the low frequency shifts, $\Delta\nu$(OH), which indicate that formation of H-complexes ($\Delta\nu$(OH) = ν(free OH)$^-$ (ν bonded OH) * has taken place, may be used as a measure of the relative stability of the intermolecular hydrogen bonds. The enthalpy of the intermolecular H bonds ($-\Delta H$) can be calculated from the $\Delta\nu$(OH) values by use of the well-known equations [5]. Analysis of $\Delta\nu$(OH) values (table 1) leads to the conclusion that steric rather than electronic factors are responsible for the differences in the strength of self-association.

Similar stabilities of the intermolecular hydrogen bonds is characteristic for both groups of primary carbinols (the $\Delta\nu$(OH) values are higher than 400 cm^{-1}, corresponding to $-\Delta H = 6.7$ kcal/mol). Replacement by a Me group at the carbinol C atom causes a more significant decrease of the $\Delta\nu$(OH) value for nonamethyl derivatives ($\Delta\nu \leqslant 160$ cm^{-1} for Ia, $-\Delta H = 4$ kcal/mol) as compared with the values for complexes with unsubstituted Cp-rings FcCHMeOH (IIa) ($\Delta\nu = 317$ cm^{-1}, $-\Delta H = 5.6$ kcal/mol). Thus in nonamethyl derivatives of secondary carbinols, even for R = Me for which the steric requirements are the least the role of steric factors precluding the formation of intermolecular H bond becomes considerably more important. The sterically most crowded molecules (R = Mes) form the least stable intermolecular hydrogen bonds (their energy is less than 2 kcal/mol, $\Delta\nu$(OH) 55–65 cm^{-1}), and are of the OH $\cdots$ π(Mes) type. The influence of the electron-accepting properties of the substituent become evident on replacement of $R = C_6H_5$ (c) by $R = C_6F_5$ (d); however for nonamethylferrocenylcarbinols this influence is considerably less important. The differences in the stability of H complexes of the (c) and (d) type are equal to 1.0 (for II) and 0.3 (for I) kcal/mol respectively. Thus the steric hindrance caused by nine Me groups in the Cp rings and substituents R at the carbinol C-atom may lead not only to a change in the relative stability of the self-associates but also to the formation of unusual H bonds, namely those of the OH $\cdots$ π(Mes) type.

The structural features of the sterically most hindered molecule (Ie) have been elucidated by an X-ray diffraction study. The structure of the molecule is shown in Fig. 1(a), bond lengths and bond angles are listed in Tables 2 and 3. Just as in the case of decamethylferrocene [6,7] or in a number of structurally characterized derivatives of decamethylferricinium [8,9] the planes of the cyclopentadienyl rings in molecule Ie are strictly parallel (the dihedral angle is 0.5°), and the five-membered cycles are almost in the ideal staggered conformation (Fig. 1(b)). It is noteworthy that in different crystalline modifications of unsubstituted ferrocene the Cp rings were found to have different conformations [10,11]. Quite naturally the repulsion between Me groups in decamethylferrocene results in a substantial increase in the barrier to relative rotation of the five-membered cycles thus stabilizing the staggered conformation. This repulsion is somewhat reduced by small (0.02–0.06 Å) deviations of Me groups from the planes of their respective Cp rings in directions away from the metal atom. Such deviations have been observed in the structures of octa- and decamethylferrocene [6]. At the same time this structural feature cannot be accounted for by steric factors alone; it has been shown [11,12] that the orientation of the exocyclic H atoms or the substituents in the cyclic π-ligands is determined first of all by electronic effects and strongly depends on the size of the cycle. In

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* The ν(free OH) position was determined from the spectra of diluted CCl_4 solutions.

particular the deviations of Me groups away from the metal atom in Ie are consistent with the general trend in the geometry of substitution in the five-membered cycles of π-cyclopentadienyl ligands, which is corroborated by the results of quantum-chemical calculations [11,12].

The C(20)–O bond is almost coplanar with the Cp ring C(1)–C(5), the O atom being displaced from the plane by 0.069(3) Å towards the Fe atom. However the Fe $\cdots$ O distance in molecule Ie remains rather long 3.824(3) Å and in fact excludes any possibility of interaction of the Fe atom with the hydroxyl group. It should be emphasized also that the O and Fe atoms in molecule I are not drawn closer together despite the fact that closer disposition could have reduced the steric hindrance in the plane of the π-ligand. In particular, it could have relieved the repulsion between the O atom and the C(14) Me group (O $\cdots$ C(14) 2.893(5) Å) which gives rise to the considerable difference in the exocyclic angles at the C(1) and C(5) atoms (see Table 3).

As might be expected the plane of the bulky mesityl substituent is almost normal to planes of the Cp rings: the dihedral angle C(1)–C(5)/C(21)–C(26) being 86.6(1)°. The repulsion of the C(27) and C(29) Me groups by the C(20) atom leads to the increase in the C(21)C(22)C(27) and C(21)C(26)C(29) bond angles to 122.3(3) and 122.7(3)°, respectively. The inequivalence of the bond angles at the C(21) atom (C(20)C(21)C(26) 122.0(3), C(20)C(21)C(22) 119.7(3)°) is obviously caused by the repulsion between the C(29) Me group and the C(1) and C(5) atoms of the Cp ligand (C(29) $\cdots$ C(1) 3.077(5), C(29) $\cdots$ C(5) 3.351(5) Å).

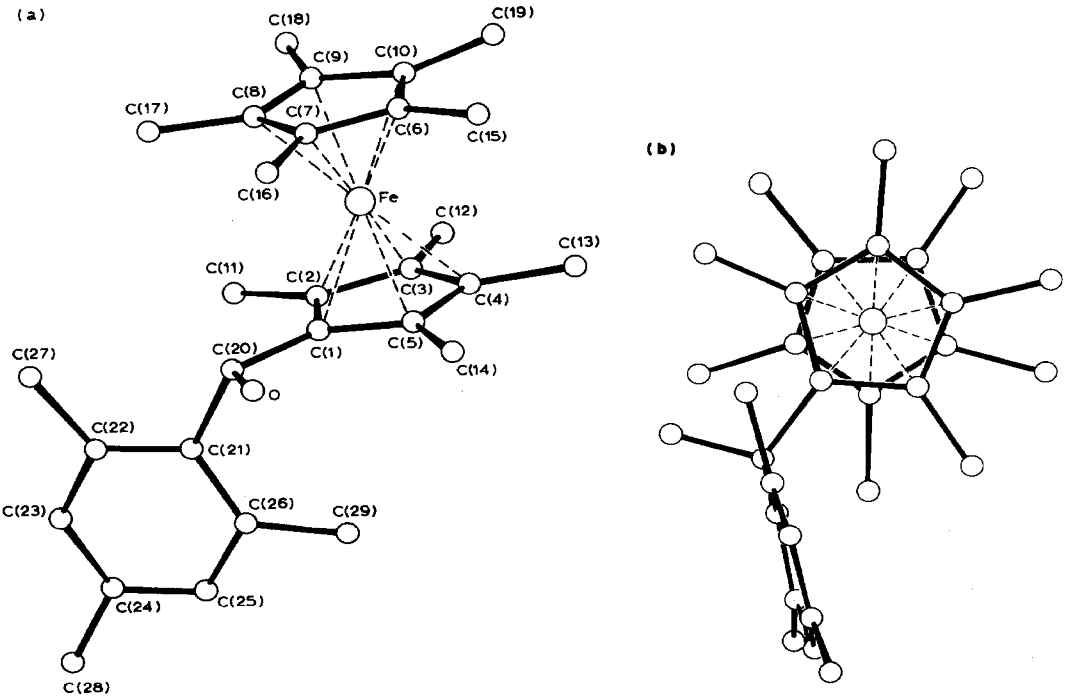

Fig. 1. The structure of ^{9}FcCHMesOH (Ie): (a) General view. (b) Projection onto the Cp*-ring plane.

Table 2

Bond lengths (Å)

Fe–C(1)	2.045(3)	C(2)–C(3)	1.427(4)	C(9)–C(10)	1.422(6)
Fe–C(2)	2.051(3)	C(2)–C(11)	1.485(4)	C(9)–C(18)	1.520(7)
Fe–C(3)	2.053(3)	C(3)–C(4)	1.414(4)	C(10)–C(19)	1.520(8)
Fe–C(4)	2.040(3)	C(3)–C(12)	1.497(4)	C(20)–C(21)	1.517(4)
Fe–C(5)	2.041(3)	C(4)–C(5)	1.431(4)	C(21)–C922)	1.402(4)
Fe–C(6)	2.035(4)	C(4)–C(13)	1.500(4)	C(21)–C(26)	1.392(4)
Fe–C(7)	2.044(4)	C(5)–C(14)	1.492(4)	C(22)–C(23)	1.388(4)
Fe–C(8)	2.023(4)	C(6)–C(7)	1.371(5)	C(22)–C(27)	1.503(5)
Fe–C(9)	2.019(5)	C(6)–C(10)	1.383(6)	C(23)–C(24)	1.366(5)
Fe–C(10)	2.023(4)	C(6)–C(15)	1.524(8)	C(24)–C(25)	1.326(5)
O–C(20)	1.424(4)	C(7)–C(8)	1.360(6)	C(24)–C(28)	1.509(6)
C(1)–C(2)	1.432(4)	C(7)–C(16)	1.529(8)	C(25)–C(26)	1.393(5)
C(1)–C(5)	1.432(4)	C(8)–C(9)	1.370(6)	C(26)–C(29)	1.502(5)
C(1)–C(20)	1.505(4)	C(8)–C(17)	1.521(7)		

It is likely that the reactivity of Ie will be affected by the steric crowding. The C(20) atom bonded to the hydroxyl group in fact turns out to be completely shielded by the C(11), C(14), C(27) and C(29) Me groups, located at 2.9–3.3 Å from it. Such an environment evidently inhibits any reactions involving attack at the carbinol carbon atom by a large particle. At the same time, the shielding by Me groups does not inhibit the generation of carbocation reaction, one which is characteristic for the ferrocenylcarbinols and proceeds by an attack on the oxygen atom by a proton in acidic medium. However, one can assume that stabilization of the reaction product, ferrocenylcarbocation, as in the case of sterically less-crowded ferrocene derivatives, will require rather close approach of the carbocationic centre to the metal atom (see review [13]), which in turn will cause even stronger repulsion between the C(27) and C(29) Me groups and the substituents in the Cp ring.

In order to investigate the possible conformations of isolated molecules of Ie not subjected to the influence of the crystalline surroundings, we carried out conforma-

Table 3

Bond angles (°)

C(2)C(1)C(5)	108.1(2)	C(7)C(6)C(15)	125.1(4)	C(1)C(20)C(21)	114.7(2)
C(2)C(1)C(20)	121.8(2)	C(10)C(6)C(15)	126.7(4)	C(20)C(21)C(22)	119.7(3)
C(5)C(1)C(20)	130.1(2)	C(6)C(7)C(8)	109.0(3)	C(20)C(21)C(26)	122.0(3)
C(1)C(2)C(3)	107.6(2)	C(6)C(7)C(16)	126.1(4)	C(22)C(21)C(26)	118.2(3)
C(1)C(2)C(11)	126.6(2)	C(8)C(7)C(16)	124.9(4)	C(21)C(22)C(23)	119.5(3)
C(3)C(2)C(11)	125.8(2)	C(7)C(8)C(9)	108.9(4)	C(21)C(22)C(27)	122.3(3)
C(2)C(3)C(4)	108.3(2)	C(7)C(8)C(17)	124.9(4)	C(23)C(22)C(27)	118.2(3)
C(2)C(3)C(12)	125.6(3)	C(9)C(8)C(17)	126.0(5)	C(22)C(23)C(24)	122.6(3)
C(4)C(3)C(12)	126.0(3)	C(8)C(9)C(10)	107.1(4)	C(23)C(24)C(25)	117.6(3)
C(3)C(4)C(5)	108.6(2)	C(8)C(9)C(18)	129.3(5)	C(23)C(24)C(28)	122.1(4)
C(3)C(4)C(13)	125.5(3)	C(10)C(9)C(18)	123.6(5)	C(25)C(24)C(28)	120.3(4)
C(5)C(4)C(13)	125.8(3)	C(6)C(10)C(9)	106.8(4)	C(24)C(25)C(26)	121.9(3)
C(1)C(5)C(4)	107.3(2)	C(6)C(10)C(19)	123.9(5)	C(21)C(26)C(25)	120.0(3)
C(1)C(5)C(14)	129.1(3)	C(9)C(10)C(19)	129.2(5)	C(21)C(26)C(29)	122.7(3)
C(4)C(5)C(14)	123.5(3)	OC(20)C(1)	109.1(2)	C(25)C(26)C(29)	117.2(3)
C(7)C(6)C(10)	108.2(3)	OC(20)C(21)	111.4(2)		

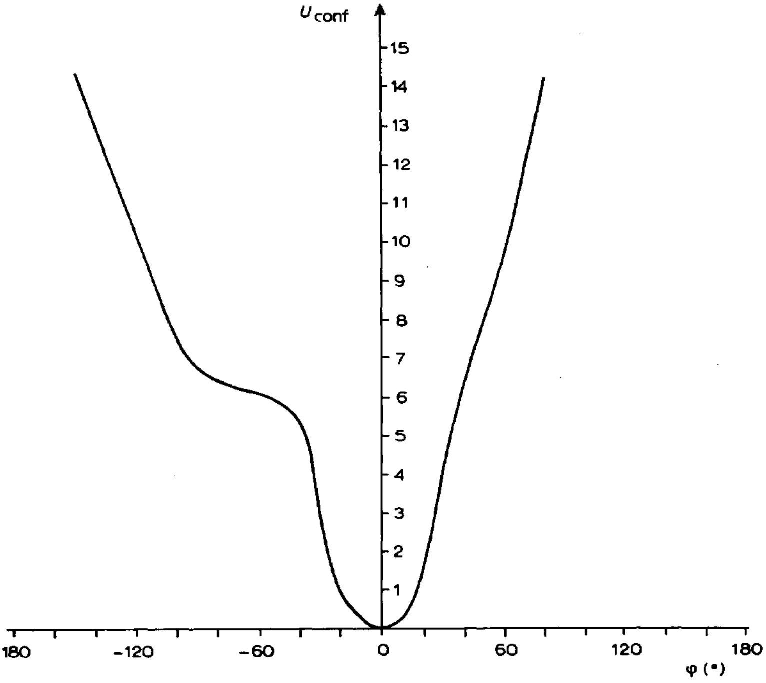

Fig. 2. The plot of conformational energy U_{conf} (kcal/mol) vs. angle of rotation ϕ (°) by carbinol group in ^{9}FeMesOH.

tional calculations in which the molecular mechanics method was used. A plot of the conformational energy vs. the C(2)C(1)C(20)O torsion angle (U_{conf}–ϕ) plot (Fig. 2) shows that only one orientation of the Mes-substituted carbinol group is possible. This orientation is close to that found in the crystal, thus in this case the crystal field, as it could be called, does not have any influence on the conformation of the molecule.

The intermolecular contacts in crystal I are characterized by the usual Van der Waals distances. The rather unfortunate shape of the molecule and the shielding of the hydroxyl group already mentioned preclude the formation of OH ··· O intermolecular hydrogen bonds. At the same time the short intermolecular contacts – of hydroxyl group with the aromatic nucleus of the mesityl substituent, HO ··· C(23) 2.29(4), HO ··· C(22) 2.69(4), HO ··· C(24) 2.87(4) Å – probably play an important role in crystal packing and thus reveal the centrosymmetric dimeric associates in crystal Ie. In contrast to the structure of tributylammonium tetraphenylborate monohydrate [14] in which the H atoms participating in the OH ··· π interaction are located symmetrically over the planes of the corresponding aromatic rings with respect to all ring atoms and the O–H bonds are at small angles to the normals to these planes, in crystal Ie the distances between the HO atom and the C(21), C(25), C(26) are longer than 3.5 Å, and the angle between the O–H bond and the normal to the aromatic plane is 48.5°. The geometry of the non-symmetric OH ··· π bond in Ie is close to that found in the 2,2-bis(2-hydroxy-5-methyl-3-t-butylphenyl)propane [15]. This fact suggests that the geometrical parameters of such H bonds may vary in a wide range owing to the diffuse nature and high polarizability of the

π-electron system. Thus the results of an X-ray diffraction study on Ie are in good agreement with the IR spectral data.

Experimental

The compounds were synthesized by procedure published previously [2]. The IR spectra were measured in Nujol and hexachlorobutadiene mixture with an IR-75 spectrophotometer.

The $(-\Delta H)$ values were calculated according to eq. 1 [5]:

$$-\Delta H = \frac{18\Delta\nu}{(\Delta\nu + 720)} \qquad (1)$$

The ν(OH) values for broad bands correspond to their centers of gravity.

Crystals of Ie are triclinic; a 8.435(2), b 8.548(3), c 18.160(6) Å, α 85.52(3), β 79.55(2), γ 76.73(2)°, V 1252.3(7) Å^3, d_{calc} 1.221 g/cm^3, $Z = 2$, space group $P\bar{1}$. The unit cell parameters and the intensities of 3714 independent reflections with $F^2 \geqslant 4\sigma$ were measured with a four-circle automatic Syntex P2_1 diffractometer (+20 °C, Mo-K_α-radiation, $\theta/2\theta$-scan, $\theta < 27°$).

Table 4

Atomic coordinates ($\times 10^4$, for Fe$\times 10^5$, for H$\times 10^3$) and their equivalent isotropic (isotropic for H atoms) thermal parameters

Atom	x	y	z	B	Atom	x	y	z	B
Fe	20130(5)	28409(5)	18078(2)	2.80(1)	O(27)	−1004(4)	2640(5)	4688(2)	6.0(1)
O	1090(4)	5604(3)	3462(1)	6.40(8)	C(28)	3284(7)	1068(7)	6336(3)	8.6(2)
C(1)	2535(3)	3214(3)	2828(1)	3.09(7)	C(29)	5639(5)	3988(6)	3912(2)	6.1(1)
C(2)	2932(3)	1529(3)	2692(1)	3.08(7)	HO	266(5)	592(5)	391(2)	9(1)
C(3)	4133(3)	1277(3)	2024(1)	3.41(7)	H(11.1)	90(7)	66(7)	342(3)	12(1)
C(4)	4465(3)	2783(4)	1747(1)	3.57(8)	H(11.2)	238(6)	−71(5)	288(2)	9(1)
C(5)	3483(3)	3997(3)	2240(1)	3.46(8)	H(11.3)	284(5)	−3(4)	349(2)	6.4(9)
C(6)	1019(4)	4214(4)	968(2)	5.0(1)	H(12.1)	583(6)	−92(6)	200(3)	11(1)
C(7)	−140(4)	4345(4)	1608(2)	5.1(1)	H(12.2)	533(5)	−12(5)	116(2)	8(1)
C(8)	−401(4)	2859(6)	1839(2)	6.1(1)	H(12.3)	430(9)	−135(8)	177(4)	16(2)
C(9)	565(6)	1757(4)	1343(3)	7.1(2)	H(13.1)	697(8)	311(7)	113(3)	12(2)
C(10)	1481(4)	2614(6)	784(2)	6.4(1)	H(13.2)	541(5)	399(5)	85(2)	8(1)
C(11)	2262(4)	258(4)	3168(2)	4.40(9)	H(13.3)	597(6)	210(6)	68(3)	10(1)
C(12)	4970(5)	−321(4)	1702(2)	5.3(1)	H(14.1)	422(5)	601(5)	241(2)	7(1)
C(13)	5702(4)	3045(5)	1070(2)	5.4(1)	H(14.2)	403(5)	594(5)	162(2)	8(1)
C(14)	3560(5)	5728(4)	2139(2)	5.2(1)	H(14.3)	256(5)	651(4)	223(2)	6.7(9)
C(15)	1610(8)	5618(8)	521(4)	11.8(3)	H(20)	22(3)	371(3)	348(1)	3.5(6)
C(16)	−1025(8)	5903(8)	2001(4)	12.0(3)	H(23)	45(4)	149(4)	583(2)	6.4(9)
C(17)	−1651(7)	2511(13)	2512(3)	15.3(4)	H(25)	493(4)	262(4)	516(2)	5.3(8)
C(18)	657(13)	−37(7)	1331(7)	19.7(6)	H(27.1)	−96(7)	193(6)	433(3)	11(2)
C(19)	2688(8)	1995(14)	87(3)	17.6(4)	H(27.2)	−159(6)	378(6)	460(3)	10(1)
C(20)	1352(4)	3895(4)	3510(2)	3.93(8)	H(27.3)	−144(6)	217(6)	506(3)	10(1)
C(21)	1854(3)	3217(4)	4252(1)	3.69(8)	H(28.1)	220(7)	127(6)	679(3)	12(1)
C(22)	741(4)	2565(4)	4789(2)	4.07(8)	H(28.2)	429(10)	142(9)	639(4)	18(2)
C(23)	1236(4)	1866(4)	5450(2)	4.8(1)	H(28.3)	407(10)	7(10)	644(4)	19(3)
C(24)	2765(4)	1821(4)	5613(2)	5.2(1)	H(29.1)	416(4)	494(4)	372(2)	5.0(7)
C(25)	3827(4)	2524(5)	5098(2)	5.4(1)	H(29.2)	561(4)	384(4)	421(2)	6.3(9)
C(26)	3398(4)	3216(4)	4421(2)	4.21(9)	H(29.3)	495(4)	336(4)	347(2)	5.9(8)

The structure was solved by the heavy-atom method. The Fe atom coordinates were found from a Patterson synthesis, all other non-hydrogen atoms were located from subsequent electron density syntheses. The refinement of the structure was carried out by use of full-matrix least squares, first isotropically and then anisotropically, which resulted in high thermal parameters for the pentamethylcyclopentadienyl ligand atoms: some components of the anisotropic temperature factors of the Me-group atoms amounted to 30–35 Å^2. High thermal parameters could have been the result of the disorder of this ligand, however all attempts to locate further positions of its atoms were unsuccessful. Therefore high thermal parameters can be explained in terms of intense thermal motion by the Cp* ligand, and the orientation of the ellipsoids indicates that the major contribution is the librational vibration of the ligand around the Fe–Cp-ring centroid axis.

All H atoms with the exception of those belonging to the Cp* ligand were located from the difference synthesis and included in the isotropic refinement, to give a final R of 0.045, and R_w of 0.059. Atomic coordinates and their thermal parameters are listed in Table 4. All calculations were carried out with an Eclipse S/200 computer with INEXTL programmes [16].

The possibility of the application of molecular mechanics method to organometallic compounds was shown in [17,18]. The conformational energy, U_{conf}, as a function of the rotation angle of carbinol group relative to the Cp* ring (ϕ) was calculated with an ES-1061 computer with a program described previously [19]. The parameters of the potentials involving the organogens were from ref. [20]. The Fe–Cp* ring centroid distance was taken from the experimental data and was not changed. The non-bonded potentials for the Fe atom were assumed to be the same as for the C atom. The φ value was changed in increments of 10°. The minimization of U_{conf} vs. all other geometric parameters of the molecule was carried out.

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