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Flash vacuum pyrolysis study of iron cyclopentadienyl complexes and the crystal structure of *O*-acetyl-*N*-(1-ferrocenylpropylidene)hydroxylamine

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Abstract

Under flash vacuum pyrolysis (FVP) conditions the acylferrocene $FcCOCMe_3$ (**1e**) [Fc = $(C_5H_5)Fe(C_5H_4)$] cracks to provide isobutene, but other acylferrocenes FcCOR (R = H, Me, Et, Me_2CH, Ph or $PhCH_2$) (**1a–d**, **f**, **g**) either were recovered unchanged or underwent total decomposition. The oxime FcCH=NOH yielded both FcCN and FcCHO while the oxime acetate yielded FcCHO and acetic acid. Other oximes FcCR=NOH were too involatile for FVP while of the oxime acetates $FcCR{=}NOCOCH_3$, no pyrolysis was observed when R = Me or Me_2CH, but when R = Et, rearrangement to FcCOEt occurred. The structure of $FcC(Et){=}NOCOCH_3$ has been determined by an X-ray diffraction study; the crystals are made up of isolated molecules with no short inter- or intra-molecular contacts.

Introduction

In a recent communication [1], we reported that flash vacuum pyrolysis (FVP) of pivaloylferrocene yields isobutene in a reaction that did not proceed by simple concerted elimination, but rather by a radical process. We have now extended this study to include a range of simple mono-acylferrocenes (**1**), their oximes (**2**), and the corresponding oxime acetates (**3**): we include also some representative di-acylferrocenes (**4**). The oxime **2a** has been shown [2] to exist in the crystalline state as a mixture of *E* and *Z* isomers, in which the molecules are coupled by hydrogen-bonding, both into dimers containing six-membered rings, R_2^2 (**6**), [3], and into extended chains: in order to investigate the *E*,*Z* isomerisation in an oxime acetate of the same series, we have determined the crystal and molecular structure of compound **3c**.

FVP of the dinuclear homometallic complexes $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ yielded [1] $(\eta^5\text{-}C_5H_5)_4Fe_4(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$, respectively, at moderate temperatures, and ferrocene and $Mo(CO)_6$ at high temperatures; we have now studied the FVP behaviour of the mixed complex $(\eta^5\text{-}C_5H_5)_2FeMo(CO)_5$.

Experimental

NMR spectra were measured at ambient temperature in $CDCl_3$ solution using a Bruker AM-300 spectrometer. The carboxaldehyde **1a** was prepared from ferrocene via *N*,*N*-dimethylaminoferrocene and ferrocenylcarbinol [4]: other monoacylferrocenes were prepared under Friedel–Crafts conditions using standard methods. Compound **1a** was converted [4] into **2a** [2], and thence into **3a**: δ(H) 2.20 (s, 3H, CH_3); 4.24 (s, 5H, C_5H_5); 4.47 (m, 2H); 4.69 (m, 2H) (C_5H_4); 8.22 (s, 1H, =C–H). δ(C) 19.8 (q, CH_3); 69.5 (d, C_5H_5); 66.7 (d); 71.2 (d); 73.3 (s) (C_5H_4); 157.0 (s, C=N); 168.8 (s, C=O). Compounds **2b** and **3b** were prepared similarly: δ(H) 2.20 (s, 3H); 2.27 (s, 3H, 2 × CH_3); 4.21 (s, 5H, C_5H_5); 4.41 (m, 2H); 4.69 (m, 2H, C_5H_4). δ(C) 14.8 (q, CH_3); 19.8 (q, CH_3); 69.5 (d, C_5H_5); 67.6 (d); 70.6 (d); 78.7 (s) (C_5H_4); 164.1 (s), 168.9 (s, C=N and C=O). For **2c**: Anal. Found: C, 60.7; H, 5.9; N, 5.5. $C_{13}H_{15}FeNO$ calc.: C, 60.6; H, 5.8; N, 5.3%. δ(H) 1.29 (t, 3H, CH_3); 2.68 (q, 2H, CH_2); 4.20 (s, 5H, C_5H_5); 4.33 (m, 2H); 4.58 (m, 2H) (C_5H_4); 10.0 (s, br, 1H, OH). δ(C) 11.7 (q, CH_3); 21.0 (t, CH_2); 69.2 (d, C_5H_5); 66.5 (d); 69.5 (d); 80.4 (s) (C_5H_4); 160.7 (s, CN). For **3c**: Anal. Found: C, 60.2; H, 5.7; N, 4.7. $C_{15}H_{17}FeNO_2$ calc.: C, 60.2; H, 5.7; N, 4.7%. δ(H) 1.27 (t, 3H, CH_2CH_3); 2.22 (s, 3H, $COCH_3$); 2.68 (q, 2H, CH_2); 4.19 (s, 5H, C_5H_5); 4.40 (m, 2H); 4.67 (m, 2H, C_5H_4). δ(C) 12.5 (q, CH_2CH_3); 20.1 (t, CH_2); 22.9 (q, $COCH_3$); 69.7 (d, C_5H_5); 67.7 (d); 70.7 (d); 78.1 (s) (C_5H_4); 169.0 (s); 169.3 (s, C=N and C=O): **2d**; and **3d**. Cyanoferrocene [5] had δ(C) 70.6 (d, C_5H_5), 70.7 (d), 71.7 (d), 72.1 (s) (C_5H_4), 120.2 (s, C≡N). $(C_5H_5)_2FeMo(CO)_5$ [6] had δ(H) 4.48 (s, 5H), 5.02 (s, 5H); δ(C) 86.1 (d); 92.5 (d, 2 × C_5H_5); 227.6 (s, CO).

Preparation of 1,1′-bis(ferrocenoyl)ferrocene

Ferrocene (1.1 g, 5.9 mmol), 1,1′-bis(chlorocarbonyl)ferrocene (2.0 g, 6.4 mmol) and anhydrous aluminium chloride (4.3 g, 32 mmol) were mixed together with dry CH_2Cl_2 (20 cm^3), and the mixture was stirred at room temperature for 6 h. After this time, examination by TLC showed that no bis(chlorocarbonyl)ferrocene was present. The mixture was hydrolysed with ice, and the organic fraction was washed with water (4 × 100 cm^3), dried, and evaporated to give the crude product. This was subjected to Soxhlet extraction with ethyl acetate; evaporation of the extract yielded the pure product (**4d**) (0.20 g, 0.33 mmol, 11.2%). δ(H) 4.17 (s, 10H, C_5H_5); 4.50 (m, 4H); 4.54 (m, 4H); 4.96 (m, 4H); 5.00 (m, 4H) (all C_5H_4). δ(C) 70.0 (d, C_5H_5); 70.6 (d); 71.8 (d); 71.9 (d); 73.7 (d); 79.9 (s); 81.6 (s) (all C_5H_4); 198.6 (s, CO). IR (CCl_4 solution): ν(CO) 1628 cm^{-1}. MS: m/z 610 (M^+, 24%); 545 [$(M-C_5H_5)^+$, 21%]; 480 [$(M-2C_5H_5)^+$, 37%]; 424 [$(C_5H_5)_4Fe_2(CO)_2^+$, 12%]; 368 [$(C_5H_4)_4Fe_2^+$, 38%]; 305 (M^{2+}, 100%).

X-Ray crystallography

Crystals of compound **3c** suitable for X-ray examination were grown from solution in CH_2Cl_2/light petroleum.

Crystal data

$C_{15}H_{17}FeNO_2$, $M_r = 299.15$, monoclinic, $a = 10.080(12)$, $b = 10.987(13)$, $c = 12.700(16)$ Å, $\beta = 97.94(10)°$, $V = 1393.0$ Å^3, space group $P2_1/n$ (non-standard no. 14), $Z = 4$, D_c 1.426 g cm^{-3}, μ(Mo-K_α) 10.15 cm^{-1}, λ 0.71069 Å, $F(000) = 616$.

Data collection

A crystal of dimensions 0.24 × 0.30 × 0.35 mm was used. Cell dimensions were determined by least-square refinement using the setting angles of 14 reflections in the range $8° \leq \theta \leq 12°$. Intensity data were collected at 22°C on a Nicolet P3 diffractometer with graphite-monochromated Mo-K_α radiation in the ω–2θ scan mode; ω scan rate 1.0–29.3° min^{-1}, ω scan width 0.6°; the maximum value of 2θ was 50°. 2730 reflections were measured, of which 2583 were unique and 1871 had $F \geq 4\sigma(F)$. Lorentz and polarisation corrections were made. The data were also corrected for absorption.

Structure solution and refinement

The structure was solved by direct methods, followed by different Fourier syntheses. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located and were included in the final refinements, with grouped isotropic temperature factors, one for the ring hydrogen atoms and another for the aliphatic hydrogen atoms: the hydrogen atoms in the two independent methyl groups were treated as riding atoms. The weighting scheme $\omega = 0.5243/[\sigma^2(F) + 0.010238(F^2)]$ gave final R and R_w values of 0.063 and 0.086, with 207 refined parameters. Scattering factor data were taken from refs. 7–9. All calculations were performed on a Prime 6350 computer using SHELX-76 [10], SHELXS [11], and XANADU [12].

Final refined coordinates are given in Table 1, and selected bond lengths and angles in Tables 2 and 3: a perspective view of the molecule, showing the atom numbering scheme, is given in Fig. 1. Tables of refined hydrogen coordinates and anisotropic temperature factors have been deposited with Cambridge Crystallographic Data Centre, and lists of observed and calculated structure factors are available from the authors.

Results and discussion

The monoacylferrocenes **1a–d** were all converted in a straightforward manner [4] to their oximes (**2**) and thence to the corresponding *O*-acetyl derivatives (**3**). It was clear from the ^{1}H and ^{13}C NMR data that compounds **2a** and **2b** both exist in solution as a mixture of *E* and *Z* isomers, as found [2] for **2a** by X-ray crystallography in the solid state, whereas **3a** and **3b** each exhibited only one form in solution. In contrast, **2c** and **3c** each exhibited only one form. Since an X-ray structural study of **3c** (see below) showed that this compound exists exclusively as the *E* isomer in the solid state, it is probable that this is the isomer observed in solution also for **3a–c**.

The formation of the diacylferrocenes, **4a** and **4b**, is straightforward: we have previously reported [13] that attempts to prepare **4c** under Friedel–Crafts conditions by use of an excess of $(CH_3)_3CCOCl/AlCl_3$ reagent leads both to acylation, with $[(CH_3)_3CCO]^+$ as the electrophile, and to alkylation by $[(CH_3)_3C]^+$, giving a

Table 1

O-Acetyl-*N*-(1-ferrocenylpropylidene)hydroxylamine: coordinates × 10^4 for non-hydrogen atoms with e.s.d.s in parentheses; $U_{eq} \times 10^3$

	x	y	z	U_{eq} [a]
Fe	1356(1)	2032(1)	6478(1)	38(1)
C1	466(5)	3683(5)	6681(4)	51(1)
C2	−478(5)	2728(6)	6659(5)	62(1)
C3	−530(5)	2103(6)	5672(5)	65(1)
C4	358(6)	2689(6)	5082(5)	60(1)
C5	983(5)	3659(5)	5693(4)	55(1)
C6	2844(5)	1746(4)	7727(4)	40(1)
C7	1872(5)	812(5)	7673(4)	51(1)
C8	1789(6)	228(5)	6676(5)	56(1)
C9	2696(5)	800(4)	6080(4)	45(1)
C10	3377(5)	1743(4)	6729(4)	41(1)
C11	4351(4)	2602(4)	6409(4)	39(1)
N12	5089(4)	3149(3)	7189(3)	43(1)
O13	5944(3)	4031(3)	6757(2)	48(1)
C14	6924(5)	4462(4)	7492(4)	47(1)
O15	7148(5)	4084(5)	8372(3)	90(1)
C16	7679(5)	5446(5)	7022(5)	60(1)
C17	4488(5)	2758(2)	5244(4)	54(1)
C18	5640(7)	2026(7)	4921(5)	86(1)

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

mixture of at least four products. The diacylferrocene **4d**, containing three ferrocene nuclei has previously been reported [14] as a minor by-product (3% yield) from the reaction of ferrocene with 1,1′-bis(chlorocarbonyl)ferrocene in chloroform solution: at least three other products were formed and the isolation of **4d** required an extensive work-up procedure. We have found, by contrast, that in dichloromethane this reaction readily provides **4d** in rather better yield (11.2%) and with a significantly easier work-up. The mass spectrum of **4d** is characterised

Table 2

O-Acetyl-*N*-(1-ferrocenylpropylidene)hydroxylamine: interatomic distances (Å)

C1–Fe	2.055(5)	C2–Fe	2.042(6)
C3–Fe	2.033(5)	C4–Fe	2.045(6)
C5–Fe	2.056(6)	C6–Fe	2.051(4)
C7–Fe	2.038(5)	C8–Fe	2.038(5)
C9–Fe	2.025(5)	C10–Fe	2.042(5)
C2–C1	1.413(8)	C5–C1	1.424(8)
C3–C2	1.424(9)	C4–C3	1.401(9)
C5–C4	1.414(8)	C7–C6	1.414(7)
C10–C6	1.443(7)	C8–C7	1.411(8)
C9–C8	1.413(8)	C10–C9	1.437(6)
C11–C10	1.460(7)	N12–C11	1.301(6)
C17–C11	1.514(7)	O13–N12	1.453(5)
C14–O13	1.348(6)	O15–C14	1.185(6)
C16–C14	1.493(8)	C18–C17	1.516(9)

Table 3

O-Acetyl-*N*-(1-ferrocenylpropylidene)hydroxylamine: selected bond angles (°)

C(1)–C(2)–C(3)	108.5(5)	C(9)–C(10)–C(11)	126.3(5)
C(2)–C(3)–C(4)	107.5(5)	C(10)–C(11)–N(12)	115.0(4)
C(3)–C(4)–C(5)	108.7(6)	C(10)–C(11)–C(17)	120.1(4)
C(4)–C(5)–C(1)	107.9(5)	N(12)–C(11)–C(17)	124.9(5)
C(5)–C(1)–C(2)	107.3(5)	C(11)–N(12)–O(13)	109.1(4)
C(6)–C(7)–C(8)	109.2(5)	N(12)–O(13)–C(14)	112.9(4)
C(7)–C(8)–C(9)	108.4(5)	O(13)–C(14)–O(15)	123.8(5)
C(8)–C(9)–C(10)	107.8(5)	O(13)–C(14)–C(16)	110.1(4)
C(9)–C(10)–C(6)	107.4(4)	O(15)–C(14)–C(16)	126.2(5)
C(10)–C(6)–C(7)	107.2(4)	C(11)–C(17)–C(18)	112.4(5)
C(6)–C(10)–C(11)	126.1(4)		

by intense peaks corresponding to the molecular ions M^+ and M^{2+}, as well as straightforward fragment ions.

FVP studies

The acylferrocene **1e** has been shown [1] to crack under FVP conditions yielding isobutene within a rather small temperature window with essentially complete recovery at lower temperatures and essentially complete decomposition at higher temperatures. We have now subjected a range of monoacylferrocenes, **1**, and

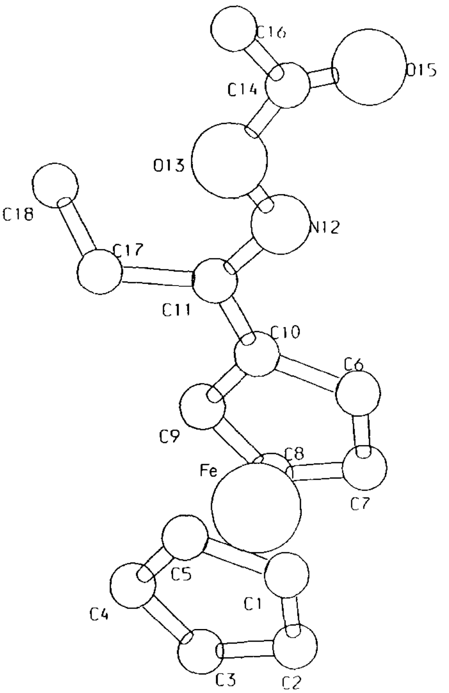
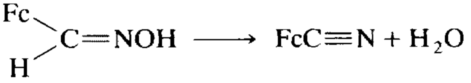


Fig. 1. Perspective view of the molecule of *O*-acetyl-*N*-(1-ferrocenylpropylidene)hydroxylamine, showing the atom numbering scheme.

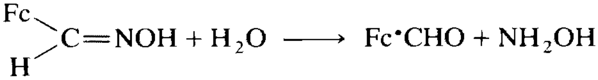
diacylferrocenes, **4**, to similar FVP investigation. None of the monoacylferrocenes, **1b**, **1c**, **1d** or **1g**, which could in principle provide unsaturated hydrocarbon products did in fact do so: in common with compounds **1a** and **1f**, recovery was essentially quantitative at temperatures below 600°C, while significant decomposition usually set in within the temperature range 650–680°C, and was generally complete by 750°C. Compound **1e** remained the sole example in which controlled cracking of the side-chain was observed. Of the diacylferrocenes, compound **4a** was recovered unchanged at furnace temperatures below 650°C, while by 800°C decomposition was complete: no other volatile products were observed. The other diacylferrocenes **4b**, **4c**, and **4d**, proved to be too involatile for FVP study.

All of the oximes **2** were found to be too involatile for FVP investigation: even the existence of 50% of the molecules of **2a** in the crystal as hydrogen-bonded dimers [2] is evidently not sufficient to allow a sufficient vapour pressure even at 200°C. When **2a** was heated beyond 200°C under reduced pressure, the sample decomposed to yield an equimolar mixture of cyanoferrocene and ferrocenecarboxaldehyde, **1a**, both of which sublimed and could be removed quantitatively. Conversion of **2a** to cyanoferrocene requires elimination of water; reaction of this with further **2a** yields **1a** and involatile hydroxylamine [Fc = $(C_5H_5)Fe(C_5H_4)$]:



$$\overset{\mathrm{Fc}}{\underset{\mathrm{H}}{>}}\mathrm{C{=}NOH} \longrightarrow \mathrm{FcC{\equiv}N} + \mathrm{H_2O}$$

(2a)



$$\overset{\mathrm{Fc}}{\underset{\mathrm{H}}{>}}\mathrm{C{=}NOH} + \mathrm{H_2O} \longrightarrow \mathrm{Fc{\cdot}CHO} + \mathrm{NH_2OH} \qquad (1)$$

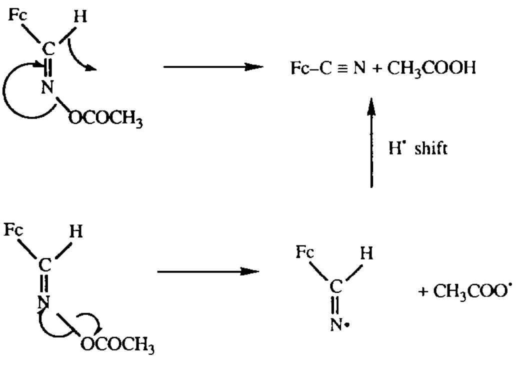
(2a) **(1a)**

The oxime acetates (**3**) are much more volatile than the parent oximes (**2**), because of their inability to form hydrogen bonds; because of the very low bond dissociation energy of the N–O single bond, they afford the possibility of forming, under FVP conditions, the nitrogen-centred radicals Fc(R)C=N•. FVP of compound **3a** produced cyanoferrocene and acetic acid; two possible mechanisms are a concerted intra-molecular elimination, or a homolytic N–O bond cleavage to form the radical Fc(R)C=N• (R = H), followed by hydrogen abstraction (Scheme 1).

The replacement of the hydrogen substituent in **3a** by an alkyl group may be expected to prevent the intra-molecular elimination of acetic acid. Accordingly, when the compounds **3b** or **3d** were subjected to FVP conditions, they both simply sublimed and were removed unchanged at all temperatures below the onset of complete pyrolytic decomposition. This effectively rules out the thermal cleavage of the N–O bonds in **2** or **3** as a synthetically useful procedure.

However FVP of compound **3c** resulted in complete conversion to the acylferrocene **1c** at furnace temperatures as low as 400°C. This conversion was entirely reproducible and particular care was taken to eliminate any possibility of a hydrolytic reaction.

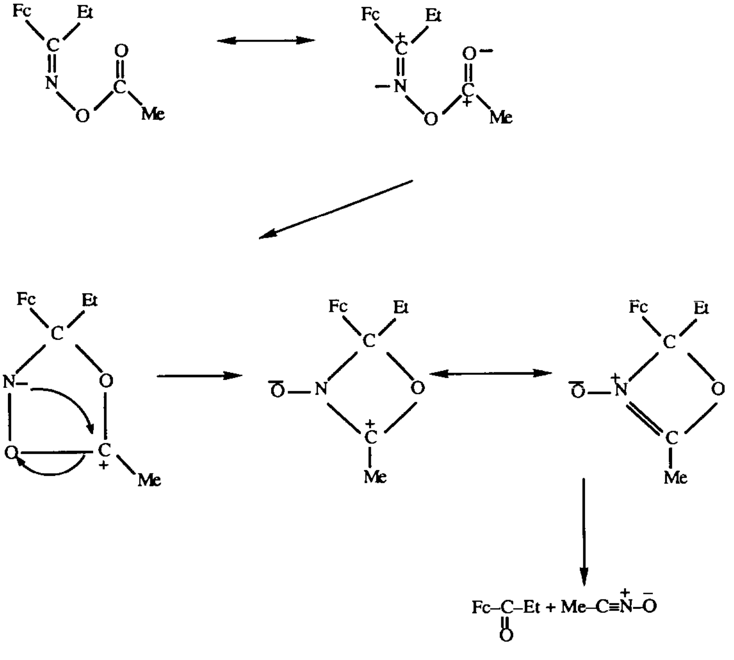
A possible rationalisation of this process, based on the assumption that only unimolecular processes are significant under FVP conditions and utilising the



Scheme 1.

charge distribution of the C=O and C=N bonds in **3c** as deduced from MNDO [15] calculations on model systems, is shown in Scheme 2.

The dinuclear complex $(C_5H_5)_2Fe_2(CO)_4$ provides the tetranuclear complex $(C_5H_5)_4Fe_4(\mu_3\text{-}CO)_4$ on FVP at 500°C, together with ferrocene, which is the sole product at higher temperatures [1]; in contrast the dinuclear molybdenum analogue $(C_5H_5)_2Mo_2(CO)_6$ produces, at 350°C, the triple Mo≡Mo bonded $(C_5H_5)_2Mo_2(CO)_4$, with $Mo(CO)_6$ as the only tractable molybdenum complex at higher temperatures [1]. This difference in FVP behaviour between $(C_5H_5)_2Fe_2(CO)_4$ and $(C_5H_5)_2Mo_2(CO)_6$ has prompted us to investigate the mixed dinuclear product $(C_5H_5)_2FeMo(CO)_5$ [6]. This complex was involatile



Scheme 2.

under vacuum at 200°C, while at temperatures above about 300°C, reversion to the two homonuclear dimers was observed. Since the mixed dimer was involatile at all temperatures at which reversion to the dimer mixture did not occur, subsequent investigations were carried out on an intimate mixture of the two dimers $(C_5H_5)_2Fe_2(CO)_4$ and $(C_5H_5)_2Mo_2(CO)_6$, prepared by rapid drying of benzene solutions of the components. At 350°C, the mixture passed through the furnace unchanged; as the furnace temperature was steadily raised, the conversion of $(C_5H_5)_2Mo_2(CO)_6$ to $(C_5H_5)_2Mo_2(CO)_4$ and thence to $Mo(CO)_6$ was initiated at a lower temperature than the conversion of $(C_5H_5)_2Fe_2(CO)_4$ to $(C_5H_5)_4Fe_4(CO)_4$ and thence to ferrocene. However the observations from a series of FVP runs undertaken throughout the temperature range 350–600°C indicated that neither of the individual homometallic dimers interacted with the other, but that the two components behaved just as they did in isolation.

Crystal and molecular structure of compound **3c**

In an attempt to understand the anomalous FVP behaviour of compound **3c**, we have determined its structure.

The structure consists of isolated molecules of exclusively *E* configuration: in this it differs markedly from that [2] of compound **2a**. Within the ferrocenyl fragment, the mean Fe–C and C–C distances for the two independent rings are identical within experimental error. The cyclopentadiene rings are in the fully eclipsed conformation. In the side chain $C(C_2H_5)=NOCOCH_3$, the heavy atoms are essentially co-planar, except for the terminal carbon atom of the ethyl group; the dihedral angles C(10)–C(11)–C(17)–C(18) and N(12)–C(11)–C(17)–C–(18) are −98.0 and 79.0°, respectively.

The C=N and N–O bonds in the side chain are both long, 1.301(7) and 1.453(5) Å; both values are greater than the upper quartile values, 1.288 and 1.408 Å, respectively, for a sample of 67 various oximes [16], and longer also than the corresponding values in simple organic oxime acetates [17,18].

There are no close inter-molecular contacts. There are no features in the structure which can assist in the interpretation of the unusual FVP behaviour of compound **3c**: in particular there are no close intra-molecular contacts involving the carbonyl oxygen atom.

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