

Formation of novel unsaturated fluorinated ligands by metal induced C–C coupling reaction of difluoroallene with fluoromethylidyne ligands of $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$

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Abstract

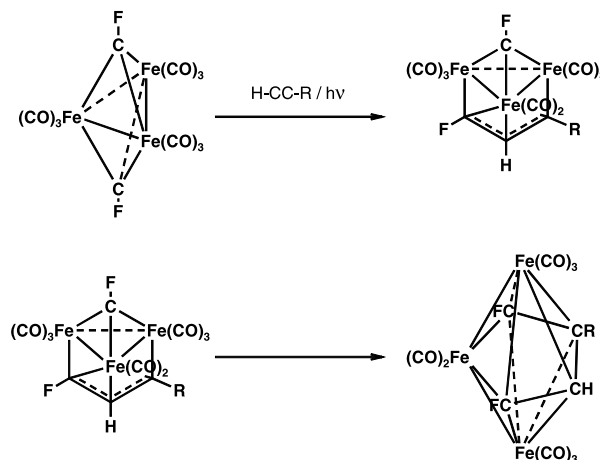
Nonacarbonyl-bis(μ_3 -fluoromethylidyne)triiron reacts with 1,1-difluoroallene forming the cluster compounds octacarbonyl(μ_3 -fluoromethylidyne)-(μ - η^1 : η^3 : η^1 -1,3-difluoro-2-fluoromethylpropane-1,2,3-triyl)triiron (**1**) and nonacarbonyl(μ - η^1 : η^2 : η^1 -1-fluoro-2-trifluoromethylbut-1-en-1-yl-4-ylidyne)triiron (**2**). The crystal and molecular structures of both compounds were elucidated by X-ray crystallography. The diferraallyl structure of **1** is similar to that of the products obtained in the reaction of $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$ with various alkynes. However, the formation of **1** requires the migration of fluorine from the CF_2 group to the CH_2 group forming a difluoromethyl substituent during or after the C–C coupling between the fluoromethylidyne group and the central carbon atom of 1,1-difluoroallene. During the even more complex formation of **2**, two carbon carbon bonds between the fluoromethylidyne groups and the allene are formed. Additionally the trifluoromethyl group of **2** is formed by a 1,4-fluorine migration. The unusual 1-fluoro-2-trifluoromethylbut-1-en-1-yl-4-ylidyne ligand bridges a very unsymmetrical triangle of iron atoms with Fe–Fe distances between 2.4917(2) and 2.7497(2) Å, respectively. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron cluster; Carbonyl ligands; Fluoromethylidyne ligands; Allyl ligands

1. Introduction

Bisalkylidyne cluster compounds of iron offer a rich organometallic chemistry [1] which was studied in detail by us and others. Carbon carbon coupling reactions with alkynes result in the formation of diferraallyl [2] or ferrol [3,4] cluster compounds. The reaction with phosphalkynes leads to the formation of phosphaferrul clusters [5] which themselves can act as ligands. The first difluoroethyne complex was obtained by a carbon carbon bond formation in the cluster expansion reaction of $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$ with $\text{Cp}^*\text{Co}(\text{CO})_2$ [6]. Reaction of the activated C–F bond of $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$ with Lewis acids enables the synthesis of substituted bisalkylidyne cluster compounds from $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$ [7]. Recently, we have demonstrated that

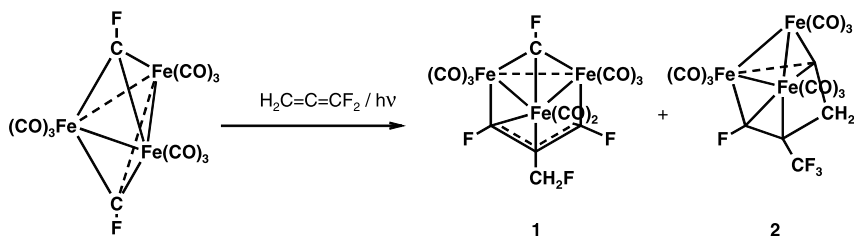
fluorinated allenes, like 1,1-difluoroallene and tetrafluoroallene are strong π accepting ligands [8]. The metal induced C–C coupling of 1,1-difluoroallene and tetrafluoroallene in the presence of decacarbonyldiman-



Scheme 1.

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Scheme 2.

gene and octacarbonyldicobalt allow the generation of more complex ligands [9]. Herein we report on the synthesis of fluorocarbon ligands by carbon carbon coupling and fluorine migration on a triiron cluster framework. This reaction is of importance in the view of a non-destructive C–F bond activation [10] as the C–F bond ($D(\text{C–F}) = 109\text{--}130 \text{ kcal mol}^{-1}$) is the strongest carbon element bond.

2. Results and discussion

Nonacarbonyl-bis(μ₃-fluoromethylidyne)triiron reacts with various alkynes in a regioselective photochemical reaction forming diferraallyl cluster compounds which can rearrange thermally to dinuclear and trinuclear ferroles as outlined in Scheme 1 [2,4]. However, no reactions of nonacarbonyl-bis(μ₃-fluoromethylidyne)triiron with alkenes has been reported thus far. In the reaction of 1,1-difluoroallene with nonacarbonyl-bis(μ₃-fluoromethylidyne)triiron two products were isolated besides unreacted starting material (Scheme 2).

Again no simple carbonyl substitution product could be detected. Both products are formed by carbon carbon coupling between the allene and one or both fluoromethylidyne units. Formally octacarbonyl(μ₃-fluoromethylidyne)-(μ-η¹:η³:η¹-1,3-difluoro-2-fluoromethylpropane-1,2,3-triyl)triiron (**1**) corresponds to the expected product of the reaction of nonacarbonyl(μ₃-fluoromethylidyne)triiron with the isomeric alkyne 1,3-difluoropropyne, F–C≡C–CH₂F. As F–C≡C–CH₂F is expected to be thermodynamically less stable than 1,1-difluoroallene the formation of **1** from 1,3-difluoropropyne is very unlikely. However, the formation of **1** requires the breaking and formation of C–F bonds. Thus we can assume that the isomerization occurs after the coordination of the allene at the iron and the migration of the fluorine atom forming the observed product **1** is catalyzed by iron which activates the very strong C–F bond.

The pathway to the second product nonacarbonyl(μ-η¹:η²:η¹-1-fluoro-2-trifluoromethylbut-1-en-1-yl-4-ylidyne)triiron (**2**) must be even more complex. The product requires the formation of two new carbon

carbon bonds and migration of fluorine to obtain the trifluoromethyl substituent.

The spectroscopic data of **1** and **2** are in perfect agreement with the structures elucidated by X-ray crystallography. The mass spectra of **1** and **2** exhibit signals for the molecular ion and fragment ions due to successive loss of carbonyl ligands. The ¹⁹F-NMR spectrum of **1** exhibits signals at 93.62 (1F, s, μ₃-CF), –18.42 (2F, s, C–CF) and –200.93 (1F, t, ²J_{HF} = 50.3 Hz; CH₂F), respectively. The resonance of the fluoromethylidyne fluorine atom shows the typical high field shift also observed in other fluoromethylidyne cluster compounds [3,11,12]. The ¹H-NMR spectrum exhibits a doublet of triplets (⁴J_{H–F} = 2 Hz) at 5.17 ppm.

Due to the C₁ symmetry of **2** the methylene hydrogen atoms of the CH₂ group are chemically non-equivalent giving rise to an AB pattern (4.59 and 4.74 ppm, ²J_{H–H} = 13 Hz) in the ¹H-NMR spectrum. The ¹⁹F-NMR spectrum consists of two signals at δ = –24.83 (1F, qua, ⁴J_{F–F} = 13.0 Hz, CF), –60.58 (3F, d, ⁴J_{H–F} = 13 Hz, CF₃) ppm. The ¹³C-{¹⁹F}-NMR spectrum of **2** exhibits six signals at 282.0, 222.3, 222.1, 205.0, 123.3 (s, CF₃), 56.7 (t, ¹J_{CH} = 141.9 Hz; CH₂) ppm.

The molecular structure of **1** is depicted in Fig. 1. The isosceles iron triangle (Fe1–Fe3 2.491(1), Fe2–Fe3 2.500(1) and Fe1–Fe2 2.600(1) Å) is capped by an unsymmetrically bound fluoromethylidyne ligand with iron carbon distances of Fe1–C1 1.997(2), Fe2–C1 1.988(2) and Fe3–C1 1.783(2) Å, respectively. Iron carbon distances to the (μ-η¹:η³:η¹-1,3-difluoro-2-fluoromethylpropane-1,2,3-triyl) ligand range from 1.961(2) to 2.180(2) Å. The structure of **1** is very similar to that of other diferraallyl clusters studied by X-ray crystallography [2] (Table 1).

Fig. 2 shows the molecular structure of **2**. To the best of our knowledge the structure of **2** is unique thus far. The cluster compound consists out of very unsymmetric triangle of iron atoms with iron iron distances ranging from 2.4917 (2) (Fe1–Fe2) to 2.7497(2) Å (Table 2).

Consequently, the Fe–Fe bond angles range from 54.98(1) to 64.66(1)°. The μ-η¹:η²:η¹-1-fluoro-2-trifluoromethylbut-1-en-1-yl-4-ylidyne ligand contains three differently coordinated carbon atoms. Again the

alkylidyne carbon atom is unsymmetrically bound to the three iron (Fe3–C1 1.771(1), Fe2–C1 1.958, Fe1–C1 2.115 Å). In this case the difference between the shortest and the longest carbon iron distances reaches 0.344 Å. C2 has no short carbon iron contacts and the alkyl type carbon atom C3 has only a very long iron carbon bond (Fe1–C3 2.179(1) Å) to Fe1. The alkylidene type carbon atom C4 is unsymmetrically bridging Fe1 and Fe2 with distances of 2.081(1) and 1.937(1) Å, respectively. Due to the coordination the bond angle at the non-coordinated carbon atom C2 becomes extremely

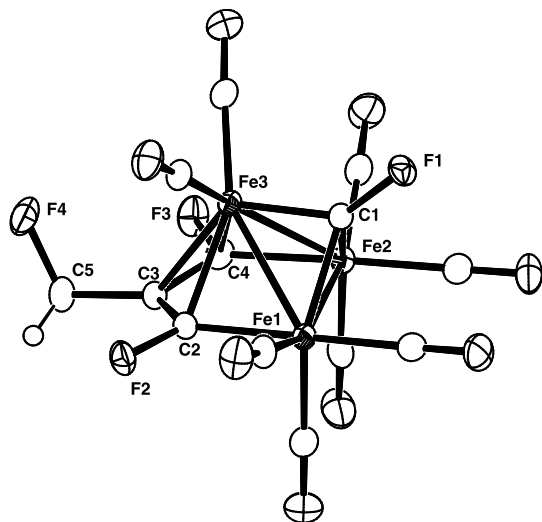


Fig. 1. Molecular structure (ORTEP [15]) of octacarbonyl(μ_3 -fluoromethylidyne)-(μ - η^1 : η^3 : η^1 -1,3-difluoro-2-fluoromethylpropane-1,2,3-triyl)triiron (**1**).

Table 1
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths		Bond angles	
Fe1–C2	1.960(2)	C2–Fe1–C1	97.80(8)
Fe1–C1	1.996(2)	Fe3–Fe1–Fe2	58.770(11)
Fe1–Fe3	2.4908(4)	C4–Fe2–C1	97.25(8)
Fe1–Fe2	2.5997(4)	Fe3–Fe2–Fe1	58.440(11)
Fe2–C4	1.961(2)	C1–Fe3–C2	102.26(9)
Fe2–C1	1.988(2)	C4–Fe3–C2	69.73(9)
Fe2–Fe3	2.4996(4)	C1–Fe3–C3	123.35(9)
Fe3–C1	1.7825(19)	C4–Fe3–C3	38.94(8)
Fe3–C4	2.026(2)	C2–Fe3–C3	38.91(8)
Fe3–C2	2.042(2)	Fe1–Fe3–Fe2	62.790(13)
Fe3–C3	2.180(2)	Fe3–C1–Fe2	82.86(8)
C1–F1	1.342(2)	Fe3–C1–Fe1	82.26(8)
C2–F2	1.364(2)	Fe2–C1–Fe1	81.46(8)
C2–C3	1.412(3)	F2–C2–C3	113.60(17)
C3–C4	1.410(3)	C4–C3–C2	110.99(18)
C3–C5	1.508(3)	C4–C3–C5	123.9(2)
C4–F3	1.365(2)	C2–C3–C5	124.4(2)
C5–F4	1.394(3)	F3–C4–C3	114.19(17)
		F4–C5–C3	110.46(18)

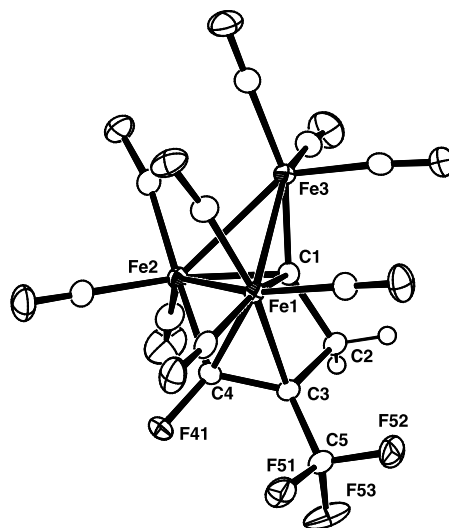


Fig. 2. Molecular structure (ORTEP [15]) of nonacarbonyl(μ - η^1 : η^2 : η^1 -1-fluoro-2-trifluoromethylbut-1-en-1-yl-4-ylidyne)triiron (**2**).

Table 2
Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths		Bond angles	
Fe1–Fe2	2.4917(2)	Fe2–Fe1–Fe3	60.355(7)
Fe1–Fe3	2.7497(2)	Fe1–Fe2–Fe3	64.661(6)
Fe2–Fe3	2.6442(3)	Fe2–Fe3–Fe1	54.983(6)
Fe1–C4	2.0813(11)	C2–C1–Fe3	148.95(8)
Fe1–C1	2.1151(11)	C2–C1–Fe2	120.87(8)
Fe1–C3	2.1791(11)	Fe3–C1–Fe2	90.18(5)
Fe2–C1	1.9577(11)	C2–C1–Fe1	98.20(7)
Fe2–C4	1.9370(11)	Fe3–C1–Fe1	89.61(5)
Fe3–C1	1.7713(11)	Fe2–C1–Fe1	75.33(4)
C1–C2	1.4905(15)	C1–C2–C3	93.86(8)
C2–C3	1.5170(15)	C4–C3–C5	125.16(10)
C3–C4	1.4128(15)	C4–C3–C2	111.77(9)
C3–C5	1.4941(15)	C5–C3–C2	119.12(9)
C4–F41	1.3666(13)		
C5–F51	1.3305(14)		
C5–F52	1.3454(14)		
C5–F53	1.3369(15)		

small C1–C2–C3 93.86(2)° whereas the H1–C2–H2 bond angle of 109.1(13)° is absolutely normal. As expected the carbon carbon bond distances C3–C4 of 1.413(2) Å is shorter than the single bonds which are C1–C2 1.491(2) and C2–C3 1.517(2) Å. The sum of the bond angles at C3 of 356.05° demonstrates that C3 has an almost planar environment of carbon atoms.

3. Experimental

Nonacarbonylbis(μ_3 -fluoromethylidyne)triiron [12] and 1,1-difluoroallene [13] were prepared by cited published procedures. All reactions were carried out in dry solvents under Ar by standard Schlenk and vacuum-line techniques.

The NMR spectra were recorded using a JEOL Lambda FX400 (400 MHz) spectrometer. Infrared spectra were measured using a Perkin–Elmer 883 e.g. 983 instrument. Mass spectra were recorded with a Varian MAT 711 (70 eV) spectrometer.

3.1. Octacarbonyl(μ_3 -fluoromethylidyne)-(μ - η^1 : η^3 : η^1 -1,3-difluoro-2-fluoromethylpropane-1,2,3-triyl)triiron (**1**) and nonacarbonyl(μ - η^1 : η^2 : η^1 -1-fluoro-2-trifluoromethylbut-1-en-1-yl-4-ylidyne)triiron (**2**)

Nonacarbonylbis(μ_3 -fluoromethylidyne)triiron (756 mg (1.57 mmol)) was dissolved in 100 ml *n*-pentane within a photoreactor. 1,1-Difluoroallene (13.7 mmol) was condensed onto this mixture using a conventional glass vacuum line system and liquid nitrogen cooling. After warming to ambient temperature the reaction mixture was irradiated with Pyrex glass filtered UV light (Philipps HPK 125 W) for 4 h. During the reaction, the color of the solution changed from orange to dark green. The solution was transferred into a 250 ml flask and silica (5 g) was added. The solvent was

evaporated under vacuum using a rotary evaporator. Column chromatography of the residue (silica, $l = 50$ cm, $d = 3$ cm) using pentane as an eluant gave an orange fraction containing the starting material and two dark green fractions. Crystallization of the first green fraction from pentane at -30 °C yielded **2** (80 mg, 9.1%) as dark green crystals, m.p. 117 °C. ^1H NMR (CDCl_3): $\delta = 4.59$ (d, CH_2 , $^2J_{\text{H-H}} = 13$ Hz), 4.74 (d, CH_2 , $^2J_{\text{H-H}} = 13$ Hz). ^{19}F NMR (CDCl_3): $\delta = -24.83$ (1F, qua, $^4J_{\text{F-F}} = 13.0$ Hz, CF), -60.58 (3F, d, $^4J_{\text{H-F}} = 13$ Hz, CF_3). ^{13}C - $\{^{19}\text{F}\}$ -NMR (CDCl_3): $\delta = 282.0$, 222.3, 222.1, 205.0, 123.3 (s, CF_3), 56.7 (t, $^1J_{\text{CH}} = 141.9$ Hz; CH_2). IR (*n*-pentane, cm^{-1}): $\tilde{\nu} = 2098$ m (CO), 2062 s (CO), 2057 s (CO), 2033 s (CO), 2027 s (CO). IR (KBr, cm^{-1}): $\tilde{\nu} = 3890$ w, 2923 w, 2849 w, 2101 s (CO), 2079 vs (CO), 2051 vs (CO), 2012 vs (CO), 1956 vs (CO), 1652 w, 1449 m, 1415 m, 1292 s, 1257 m, 1187 w, 1156 m, 1134 m, 1125 w, 1077 m, 1055 m, 978 w, 813 m, 742 w, 679 m, 652 m, 621 m, 598 m, 569 s, 550 w, 535 w, 492 w, 474 w, 412 w, 373 w. MS (70 eV); $m/z = 558$ (7%, M^+), 530 (3%, $\text{M}^+ - \text{CO}$), 502 (83%, $\text{M}^+ - 2\text{CO}$), 474 (16%, $\text{M}^+ - 3\text{CO}$), 446 (27%, $\text{M}^+ - 4\text{CO}$),

Table 3
Crystal data and structure refinement parameters for octacarbonyl(μ_3 -fluoromethylidyne)-(μ - η^1 : η^3 : η^1 -1,3-difluoro-2-fluoromethylpropane-1,2,3-triyl)triiron (**1**) and nonacarbonyl(μ - η^1 : η^2 : η^1 -1-fluoro-2-trifluoromethylbut-1-en-1-yl-4-ylidyne)triiron (**2**)

	1	2
Empirical formula	$\text{C}_{13}\text{H}_2\text{F}_4\text{Fe}_3\text{O}_8$	$\text{C}_{14}\text{H}_2\text{F}_4\text{Fe}_3\text{O}_9$
Formula weight	529.70	557.71
Temperature (K)	133(2)	133(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
<i>a</i> (Å)	14.0262(8)	8.7564(5)
<i>b</i> (Å)	8.7723(5)	13.2156(8)
<i>c</i> (Å)	14.1255(8)	15.1967(9)
α (°)	90	90
β (°)	110.550(1)	90.334(1)
γ (°)	90	90
<i>V</i> (Å ³)	1627.43(16)	1758.55(18)
<i>Z</i>	4	4
D_{calc} (Mg m^{-3})	2.162	2.106
Absorption coefficient (mm^{-1})	2.725	2.532
<i>F</i> (000)	1032	1088
Crystal size (mm^3)	$0.59 \times 0.31 \times 0.05$	$0.75 \times 0.5 \times 0.3$
Theta range for data collection (°)	2.54–31.42	2.04–31.40
Index ranges	$-19 \leq h \leq 20$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$	$-12 \leq h \leq 12$, $-19 \leq k \leq 19$, $-22 \leq l \leq 22$
Reflections collected	18972	20984
Independent reflections	5020 [$R_{\text{int}} = 0.0392$]	5430 [$R_{\text{int}} = 0.0172$]
Completeness to $\theta = 25.00^\circ$	93.3%	93.4%
Absorption correction	Empirical SADABS	Empirical SADABS
Max/min transmission	1.0000, 0.7675	0.494, 0.376
Refinement method	Full-matrix least-squares on F^2 , SHELXL-97	Full-matrix least-squares on F^2 , SHELXL-97
Data/restraints/parameters	5020/0/261	5430/0/279
Goodness-of-fit on F^2	1.087	1.118
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0305$, $wR_2 = 0.0801$	$R_1 = 0.0196$, $wR_2 = 0.0516$
<i>R</i> indices (all data)	$R_1 = 0.0410$, $wR_2 = 0.0835$	$R_1 = 0.0215$, $wR_2 = 0.0524$
Largest difference peak and hole ($\text{e} \text{ \AA}^{-3}$)	0.646 and -0.443	0.425 and -0.502

418 (40%, $M^+ - 5CO$), 390 (100%, $M^+ - 6CO$), 362 (75%, $M^+ - 7CO$), 334 (70%, $M^+ - 8CO$), 306 (90%, $M^+ - 9CO$). Anal. Calc. for $C_{14}H_2F_4O_9Fe_3$ (557.70 g mol⁻¹): C, 30.15; H, 0.36. Found: C, 30.71; H, 1.26%.

Crystallization of the second green fraction from pentane at $-30\text{ }^\circ\text{C}$ yielded **1** (50 mg, 6.0%) as dark green crystals, m.p. $136\text{ }^\circ\text{C}$. ¹H-NMR ($CDCl_3$): $\delta = 5.17$ (2H, td, $^2J_{HF} = 50.3$ Hz, $^4J_{HF} = 1.8$ Hz; CH_2F). ¹⁹F-NMR ($CDCl_3$): $\delta = 93.62$ (1F, s, μ_3 -CF), -18.42 (2F, s, C-CF), -200.93 (1F, t, $^2J_{HF} = 50.3$ Hz; CH_2F). IR (KBr, cm^{-1}): $\tilde{\nu} = 2973$ w, 2097 s (CO), 2043 vs (CO), 2013 s (CO), 1463 w, 1427 w, 1389 s, 1368 m, 1262 w, 1239 m, 1167 s, 1128 vs, 1034 s, 1034 s, 1010 s, 994 m, 915 m, 715 m, 699 m, 663 s, 613 s, 594 vs, 573 s, 528 s, 497 m, 448 m, 431 m, 408 m, 382 w, 318 w, 295 w. IR (*n*-pentane, cm^{-1}): $\tilde{\nu} = 2097$ w (CO), 2054 vs (CO), 2036 m (CO), 2021 m (CO). MS (70 eV); $m/z = 530$ (23%, M^+), 502 (60%, $M^+ - CO$), 474 (29%, $M^+ - 2CO$), 446 (32%, $M^+ - 3CO$), 418 (31%, $M^+ - 4CO$), 390 (23%, $M^+ - 5CO$), 362 (12%, $M^+ - 6CO$), 334 (27%, $M^+ - 7CO$), 306 (51%, $M^+ - 8CO$). Anal. Calc. for $C_{13}H_2F_4O_8Fe_3$ (529.69 g mol⁻¹): C, 29.48; H, 0.4. Found: C, 29.54; H, 0.83%.

3.2. X-ray crystallographic study

Suitable crystals of **1** and **2** were obtained by crystallization from *n*-pentane–dichloromethane at $-20\text{ }^\circ\text{C}$. Details on the data collection, structure solution and refinement are summarized in Table 3.

Data collection: Bruker-AXS, SMART 1000, Mo- K_{α} , ω scan. Structure solution by direct methods (SHELXS-97 [14]), structure refinement, full-matrix least-squares on F_o^2 (SHELXL-97 [14]) using anisotropic thermal parameters for non-hydrogen atoms, hydrogen atoms were located in the difference Fourier map and refined using isotropic thermal parameters. ORTEP [15] was used for molecular drawings.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 169553 and 169554 for compounds (**1**) and (**2**), respectively. Copies of this informa-

tion may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

Acknowledgements

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