

Structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2\text{Fe}_2(\text{CO})_8(\mu_2\text{-CO})(\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6)$: an unusual mixed-metal compound containing a bridging diallyl ligand derived by unsymmetrical coupling of two allenyl groups¹

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Abstract

The heteronuclear compound $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2\text{Fe}_2(\text{CO})_8(\mu_2\text{-CO})(\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6)$ (**1**), obtained by reaction of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$ with $\text{Fe}_2(\text{CO})_9$, displays unusually complex ¹H and ¹³C NMR spectra. All nine CO ligands, as well as all six carbon and hydrogen atoms of C_6H_6 , afford separate resonance signals. The structure of **1** was determined by X-ray diffraction techniques. The complex crystallizes from hexane (as a 3:1 cluster:solvate complex) in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 7.852(1)$ Å, $b = 23.487(5)$ Å, $c = 24.144(4)$ Å, $\alpha = 74.47(2)^\circ$, $\beta = 84.79(1)^\circ$, $\gamma = 86.69(1)^\circ$, $V = 4269.8(14)$ Å³. The unit cell contains six polynuclear Ru_2Fe_2 -containing molecules and two molecules of hexane. X-ray diffraction data (Mo K α , $2\theta = 7.0\text{--}40.0^\circ$) were collected with a Siemens R3m/V diffractometer and the structure was refined to $R = 6.56\%$ for all 7987 independent reflections ($R = 2.90\%$ for those 4844 reflections with $|F_o| > 6\sigma(|F_o|)$). The organometallic molecule is based upon an unusual $\text{CH}^*\text{-C}(\text{CH}_2)\text{-CH}^*\text{-CH}_2$ fragment, which is derived from a β - γ coupling of two allenyl moieties and which forms π -allyl linkages to the two iron atoms and σ -bonds (via the starred carbon atoms) to $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}$ moieties. The metal atoms are arranged as a linear $\text{Ru}(1)\text{-Fe}(2)\text{-Fe}(3)$ system and a lone $\text{Ru}(4)$ atom. Dimensions in the three independent molecules are internally consistent, with carbonyl-bridged $\text{Ru}(1)\text{-Fe}(2)$ distances of 2.687(1), 2.679(1) and 2.687(1) Å and $\text{Fe}(2)\text{-Fe}(3)$ distances of 2.895(2), 2.871(2) and 2.906(2) Å.

Keywords: Iron; Ruthenium; Allene; Allyl complexes; Coupling reaction; Crystal structure

1. Introduction

In a previous publication [1] we reported that reaction of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$ with $\text{Fe}_2(\text{CO})_9$ under various experimental conditions leads to the isolation of four mixed-metal products. The characterization of three of them, all RuFe_2 complexes, was reported in that paper. The fourth product, a tetranuclear Ru_2Fe_2 complex (**1**), occurred persistently, albeit not in high yield, under all conditions employed. Its ¹H and ¹³C NMR spectra were most unusual with respect to the number of resonances observed and the range of their chemical shifts. An X-ray diffraction study revealed a rather complex nature of the crystal of **1** (actually $\text{I}_3 \cdot \text{C}_6\text{H}_{14}$), and this complexity prompted a separate

publication of our results. Reported herein are spectroscopic properties and the solid state structure of this unusual product.

2. Experimental details

2.1. General procedures and measurements

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of Ar by use of standard procedures [2]. Solvents were purified by distillation under an Ar atmosphere prior to use. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer model 283B grating spectrophotometer and were

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¹ This paper is dedicated to Professor Marvin D. Rausch on the occasion of his 65th birthday.

calibrated with polystyrene. ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-250 spectrometer, and the chemical shifts are given in ppm downfield from Me_4Si . Fast atom bombardment (FAB) mass spectra were recorded on a VG70-250S spectrometer by Mr. David C. Chang.

2.2 Preparation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2\text{Fe}_2(\text{CO})_8(\mu_2\text{-CO})(\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6)_3$ (**1**)

Complex **1** was obtained as a red-purple crystalline solid by reaction of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$ with an excess of $\text{Fe}_2(\text{CO})_9$ in hexane at reflux. The synthesis and isolation are described in detail elsewhere [1]. **1**: dec. temp. 125°C . IR (CH_2Cl_2): $\nu(\text{CO})$ 2040 (s), 2021 (m), 1990 (s), 1979 (s), 1966 (m-s), 1940 (sh), 1798 (w-m), 1603 (w) cm^{-1} . ^1H NMR (acetone- d_6): δ 10.48 (d, $^4J = 3$ Hz, CH), 5.74 (s, C_5H_5), 5.64 (d, $^2J = 0.8$ Hz, CHH), 5.51 (s, C_5H_5), 2.38 (dd, $^2J = 1$ Hz, $^4J = 3$ Hz, CHH), 1.30 (dd, $^2J = 0.7$ Hz, $^4J = 3$ Hz, CHH), 0.52 (t, $^4J = 4J = 3$ Hz, CH), -0.73 (dd, $^2J = 0.9$ Hz, $^4J = 3$ Hz, CHH). ^{13}C NMR (CD_2Cl_2): δ 243.0 (d, $^3J_{\text{CH}} = 2.3$ Hz, $\mu\text{-CO}$), 221.7, 220.4 (2d, $^3J_{\text{CH}} = 2.3$ Hz, $\text{Fe}(\text{CO})_2$), 214.5, 211.9, 209.1 (3s,

Table 1
Crystallographic data for $[(\text{C}_5\text{H}_5)_2\text{Ru}_2\text{Fe}_2(\text{CO})_9(\text{C}_6\text{H}_6)_3] \cdot \text{C}_6\text{H}_{14}$

Formula weight	2408.7 [3(774.2) + 86.2]
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.852(1)
b (Å)	23.487(5)
c (Å)	24.144(4)
α (deg)	74.47(2)
β (deg)	84.79(1)
γ (deg)	86.69(1)
V (Å ³)	4269.8(14)
Z	2
$D(\text{calc'd})$ (g cm^{-3})	1.874
$F(000)$	2368
Crystal size (mm^3)	$0.2 \times 0.2 \times 0.3$
Temperature (K)	295(1)
Radiation	Mo K α ($\bar{\lambda} = 0.710730$ Å)
$\mu(\text{Mo K } \alpha)$ (cm^{-1})	20.71
Scan-type	ω
2θ range (deg)	7.0–40.0
Octants measured	$\pm h, \pm k, \pm l$
Total number of reflections collected	15974
Total number of unique reflections	7987 ($R_{\text{int}} = 2.03\%$)
Unique reflections with $I > 3\sigma(I)$	4844
Transmission factors	0.526–0.584
$R(I > 3\sigma(I))$	2.90%
$R_w(I > 3\sigma(I))$	2.88%
R (all data)	6.56%
R_w (all data)	3.77%
GOF	1.02
Max. and min. residuals in final diff. map ($\text{e } \text{Å}^{-3}$)	+0.71 -0.69

Table 2

Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq} ($\text{Å}^2 \times 10^3$) for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2\text{Fe}_2(\text{CO})_8(\mu\text{-CO})(\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6)_3] \cdot \text{C}_6\text{H}_{14}$

	x	y	z	U_{eq}^a
<i>Molecule 'a'</i>				
Ru(1a)	6379(1)	$-10(1)$	6111(1)	47(1)
Fe(2a)	4891(2)	$-764(1)$	7047(1)	41(1)
Fe(3a)	5303(2)	$-950(1)$	8263(1)	38(1)
Ru(4a)	3519(1)	188(1)	9089(1)	35(1)
C(1a)	6135(11)	3(3)	6955(3)	39(4)
C(2a)	4620(11)	6(3)	7327(4)	40(4)
C(3a)	3073(11)	$-75(3)$	7107(4)	44(4)
C(4a)	4851(10)	$-19(3)$	7938(3)	34(4)
C(5a)	3694(10)	$-243(3)$	8423(3)	32(3)
C(6a)	2703(10)	$-734(3)$	8428(3)	42(4)
C(11a)	4680(14)	556(5)	5886(4)	63(5)
O(11a)	3692(10)	926(3)	5680(3)	96(4)
C(12a)	4642(13)	$-659(4)$	6228(4)	55(4)
O(12a)	3984(10)	$-883(3)$	5921(3)	79(4)
C(21a)	6609(14)	$-1300(4)$	7069(4)	55(4)
O(21a)	7633(9)	$-1671(3)$	7079(3)	81(4)
C(22a)	3131(13)	$-1244(4)$	7192(4)	48(4)
O(22a)	1961(9)	$-1535(3)$	7275(3)	78(4)
C(31a)	4935(11)	$-1685(5)$	8230(4)	53(4)
O(31a)	4751(9)	$-2175(3)$	8257(3)	77(3)
C(32a)	5765(12)	$-1173(4)$	8993(5)	50(4)
O(32a)	6085(10)	$-1342(3)$	9466(3)	77(3)
C(33a)	7540(13)	$-877(4)$	8040(4)	48(4)
O(33a)	8959(9)	$-834(3)$	7913(3)	79(4)
C(41a)	2963(12)	$-505(5)$	9654(4)	52(5)
O(41a)	2583(9)	$-921(3)$	10008(3)	79(3)
C(42a)	5854(13)	39(3)	9169(4)	40(4)
O(42a)	7295(9)	$-34(3)$	9202(3)	60(3)
C(51a)	8248(19)	472(6)	5443(8)	94(7)
C(52a)	7827(15)	$-3(10)$	5258(5)	89(7)
C(53a)	8308(18)	$-497(6)$	5642(8)	85(7)
C(54a)	9106(16)	$-347(8)$	6056(6)	86(7)
C(55a)	9116(16)	252(10)	5944(7)	89(8)
C(61a)	1853(18)	835(5)	9446(5)	70(5)
C(62a)	3298(17)	1120(4)	9182(6)	70(6)
C(63a)	3369(13)	1142(4)	8603(5)	58(5)
C(64a)	1931(15)	885(4)	8504(5)	58(5)
C(65a)	949(12)	679(4)	9027(6)	66(5)
<i>Molecule 'b'</i>				
Ru(1b)	$-520(1)$	2791(1)	5776(1)	49(1)
Fe(2b)	$-2069(2)$	2193(1)	6781(1)	41(1)
Fe(3b)	$-1557(2)$	2229(1)	7933(1)	37(1)
Ru(4b)	$-3158(1)$	3505(1)	8600(1)	43(1)
C(1b)	$-737(12)$	2964(3)	6556(4)	46(4)
C(2b)	$-2243(12)$	3043(3)	6913(4)	41(4)
C(3b)	$-3818(11)$	2922(3)	6724(4)	47(4)
C(4b)	$-1999(10)$	3134(3)	7490(4)	42(4)
C(5b)	$-3122(10)$	2988(3)	8004(4)	39(4)
C(6b)	$-4157(10)$	2486(3)	8083(4)	42(4)
C(11b)	$-2217(14)$	3354(5)	5467(4)	61(5)
O(11b)	$-3123(11)$	3707(3)	5230(3)	95(4)
C(12b)	$-2305(12)$	2165(4)	5986(4)	52(4)
O(12b)	$-2993(10)$	1884(3)	5746(3)	80(4)
C(21b)	$-397(12)$	1624(4)	6871(4)	49(4)
O(21b)	593(10)	1244(3)	6925(3)	83(4)
C(22b)	$-3847(13)$	1736(4)	6983(4)	47(4)
O(22b)	$-5047(9)$	1445(3)	7088(3)	70(3)
C(31b)	$-2021(10)$	1477(5)	8012(4)	44(4)
O(31b)	$-2270(8)$	981(3)	8103(3)	58(3)

Table 2 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
<i>Molecule 'b'</i>				
C(32b)	−1004(11)	2096(4)	8656(4)	44(4)
O(32b)	−570(9)	1987(3)	9111(3)	72(3)
C(33b)	652(14)	2254(4)	7681(4)	49(4)
O(33b)	2091(9)	2291(3)	7542(3)	74(3)
C(41b)	−3681(12)	2844(4)	9218(4)	52(4)
O(41b)	−4059(10)	2462(3)	9600(3)	82(3)
C(42b)	−810(14)	3388(4)	8641(4)	53(4)
O(42b)	632(10)	3333(3)	8671(3)	80(4)
C(51b)	1379(16)	3137(6)	5046(5)	79(6)
C(52b)	917(14)	2613(7)	4983(5)	77(6)
C(53b)	1393(16)	2167(5)	5450(7)	87(6)
C(54b)	2229(15)	2454(9)	5803(5)	90(7)
C(55b)	2238(14)	3043(7)	5550(7)	83(7)
C(61b)	−4569(26)	4219(6)	8916(6)	93(7)
C(62b)	−3311(18)	4469(6)	8555(12)	124(11)
C(63b)	−3500(34)	4412(8)	8046(10)	155(13)
C(64b)	−4960(38)	4120(9)	8068(11)	168(16)
C(65b)	−5609(16)	4010(5)	8613(11)	115(10)
<i>Molecule 'c'</i>				
Ru(1c)	3259(1)	7167(1)	6393(1)	44(1)
Fe(2c)	1693(2)	6318(1)	7227(1)	40(1)
Fe(3c)	2052(2)	5911(1)	8459(1)	42(1)
Ru(4c)	356(1)	6918(1)	9453(12)	43(1)
C(1c)	3046(11)	7041(3)	7259(3)	43(4)
C(2c)	1545(12)	6995(3)	7638(4)	40(4)
C(3c)	−57(12)	6981(3)	7397(3)	46(4)
C(4c)	1723(10)	6849(3)	8269(3)	40(4)
C(5c)	558(11)	6581(4)	8729(4)	43(4)
C(6c)	−533(11)	6137(3)	8655(4)	49(4)
C(11c)	1578(13)	7755(4)	6245(4)	55(4)
O(11c)	626(10)	8146(3)	6077(3)	84(4)
C(12c)	1485(12)	6554(4)	6389(4)	51(4)
O(12c)	815(10)	6407(3)	6040(3)	80(4)
C(21c)	3360(12)	5785(4)	7173(4)	50(4)
O(21c)	4405(10)	5438(3)	7117(3)	79(3)
C(22c)	−117(13)	5877(4)	7268(4)	50(4)
O(22c)	−1304(10)	5621(3)	7262(3)	80(4)
C(31c)	1448(11)	5246(4)	8311(4)	47(4)
O(31c)	1032(9)	4804(3)	8254(3)	73(3)
C(32c)	2538(13)	5581(4)	9175(5)	61(5)
O(32c)	2884(11)	5332(3)	9635(3)	93(4)
C(33c)	4306(14)	5950(4)	8250(4)	53(4)
O(33c)	5752(9)	5979(3)	8135(3)	86(4)
C(41c)	−187(14)	6204(5)	9967(5)	71(5)
O(41c)	−552(12)	5774(3)	10308(3)	110(4)
C(42c)	2677(14)	6751(4)	9538(4)	53(4)
O(42c)	4107(10)	6657(3)	9569(3)	82(4)
C(51c)	5223(19)	7696(5)	5803(9)	97(7)
C(52c)	4687(14)	7306(9)	5527(4)	81(6)
C(53c)	5139(16)	6760(6)	5834(7)	77(6)
C(54c)	5952(14)	6800(7)	6298(6)	78(6)
C(55c)	6048(17)	7381(9)	6284(7)	93(8)
C(61c)	−1226(18)	7554(5)	9871(5)	78(6)
C(62c)	177(15)	7846(4)	9581(6)	70(6)
C(63c)	108(17)	7872(4)	9001(6)	75(6)
C(64c)	−1324(19)	7622(5)	8919(6)	74(6)
C(65c)	−2178(14)	7404(5)	9458(8)	81(6)

Fe(CO)₃, 203.8 (s, RuCO), 200.4, 200.2 (2s, Ru(CO)₂), 177.6 (d, ¹J_{CH} = 154 Hz, CH), 110.3 (s, C), 91.1 (m, C₅H₅), 90.3 (s, C), 89.8 (m, C₅H₅), 72.4 (d, ¹J_{CH} = 161

Table 2 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
<i>Hexane of solvation</i>				
C(1S)	13650(36)	4915(11)	4329(11)	454(23)
C(2S)	12064(38)	5024(12)	4026(12)	357(18)
C(3S)	10667(45)	5060(16)	4216(15)	584(40)
C(4S)	9658(32)	5341(11)	3718(11)	305(14)
C(5S)	7910(42)	5366(15)	3878(14)	533(30)
C(6S)	7444(33)	5755(10)	3334(10)	407(19)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Hz, CH), 61.9 (t, ¹J_{CH} = 162 Hz, CH₂), 42.7 (t, 8u1J_{CH} = 156 Hz, CH₂). FAB-MS, *m/z* (¹⁰²Ru): 776 (M⁺) then stepwise loss of nine COs. Anal. Found: C, 38.68; H, 2.29. C₂₅H₁₆Fe₂O₉Ru₂. Calc.: C, 38.76; H, 2.08%.

2.3. Crystallographic analysis

2.3.1. Collection of X-ray diffraction data for [(η⁵-C₅H₅)₂Ru₂Fe₂(CO)₈(μ-CO)(μ₄-η⁶-C₆H₆)]₃ · C₆H₁₄

Crystals of **1**₃ · C₆H₁₄ were grown from CH₂Cl₂–hexane at ca. −23°C.

The crystal used for the diffraction study was a parallelepiped of approximate dimensions 0.2 × 0.2 × 0.3 mm³. It was aligned with its extended direction essentially collinear with the instrumental ϕ -axis. Data were collected by the ω -scan method. Details of data collection are provided in Table 1. The crystal belongs to the triclinic system, possible space groups being *P*1 (*C*₁¹; No. 1) or *P* $\bar{1}$ (*C*₁¹; No. 2). Both intensity statistics and frequency of occurrence data [3] favor the centrosymmetric possibility. Space group *P* $\bar{1}$ was thus chosen and later confirmed by the successful solution of the structure in this higher symmetry space group. All data were corrected for Lorentz and polarization effects and for absorption. A total of 15 974 reflections was collected for the entire sphere ($\pm h$, $\pm k$, $\pm l$) for $2\theta = 7.0$ – 40.0° . Data were merged (*R*_{int} = 2.03%) to provide 7987 independent reflections with $|F_o| > 0.3\sigma(|F_o|)$.

2.3.2. Solution and refinement of the structure

The structure was solved by a combination of direct-methods and difference-Fourier techniques. Refinement led to convergence with *R* = 6.56%, *wR* = 3.77% and GOF = 1.02 for 7987 reflections refined against 1052 variables. (*R* = 2.90% and *wR* = 2.88% for those 4844 reflections with $I > 3\sigma(I)$.)

All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in calculated positions [4], and an unexpected solvent molecule (hexane) was found in accompaniment with three discrete, crystallographically independent, (η⁵-C₅H₅)₂Ru₂Fe₂(CO)₈(μ-CO)(μ₄-η⁶-C₆H₆) molecules.

Final atomic coordinates appear in Table 2.

3. Results and discussion

3.1. Spectroscopic properties of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2\text{Fe}_2\text{-(CO)}_8(\mu_2\text{-CO})(\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6)$ (**1**)

The molecular composition of **1** is supported by elemental analysis and FAB mass spectrometry, which

also shows fragments corresponding to a stepwise loss of nine COs. The ^{13}C NMR spectrum features nine signals in the low-field region. Those at δ 221.7, 220.4, 214.5, 211.9 and 209.1 are assigned to the FeCOs, whereas those at δ 203.8, 200.4 and 200.2 are attributed to the RuCOs [5]. The signal at δ 243.0 is assigned to a $\mu_2\text{-CO}$ [6]. In agreement with the forego-

Table 3

Bond lengths (Å) within the $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2\text{Fe}_2(\text{CO})_8(\mu\text{-CO})(\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6)]_3 \cdot \text{C}_6\text{H}_{14}$ crystal

Molecule a		Molecule b		Molecule c	
<i>Metal–metal distances</i>					
Ru(1a)–Fe(2a)	2.687(1)	Ru(1b)–Fe(2b)	2.679(1)	Ru(1c)–Fe(2c)	2.687(1)
Fe(2a)–Fe(3a)	2.895(2)	Fe(2b)–Fe(3b)	2.871(2)	Fe(2c)–Fe(3c)	2.906(2)
<i>Metal–carbonyl distances</i>					
Ru(1a)–C(11a)	1.839(10)	Ru(1b)–C(11b)	1.879(10)	Ru(1c)–C(11c)	1.841(10)
Ru(1a)–C(12a)	2.049(10)	Ru(1b)–C(12b)	2.023(9)	Ru(1c)–C(12c)	2.061(10)
Fe(2a)–C(12a)	1.953(10)	Fe(2b)–C(12b)	1.964(11)	Fe(2c)–C(12c)	1.968(10)
Fe(2a)–C(21a)	1.786(10)	Fe(2b)–C(21b)	1.802(10)	Fe(2c)–C(21c)	1.779(9)
Fe(2a)–C(22a)	1.785(10)	Fe(2b)–C(22b)	1.763(10)	Fe(2c)–C(22c)	1.786(10)
Fe(3a)–C(31a)	1.789(12)	Fe(3b)–C(31b)	1.780(11)	Fe(3c)–C(31c)	1.789(11)
Fe(3a)–C(32a)	1.764(11)	Fe(3b)–C(32b)	1.777(11)	Fe(3c)–C(32c)	1.761(11)
Fe(3a)–C(33a)	1.794(10)	Fe(3b)–C(33b)	1.784(11)	Fe(3c)–C(33c)	1.796(11)
Ru(4a)–C(41a)	1.867(9)	Ru(4b)–C(41b)	1.877(9)	Ru(4c)–C(41c)	1.847(10)
Ru(4a)–C(42a)	1.865(10)	Ru(4b)–C(42b)	1.855(11)	Ru(4c)–C(42c)	1.860(11)
<i>Metal–($\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6$) ligand distances</i>					
Ru(1a)–C(1a)	2.037(8)	Ru(1b)–C(1b)	2.023(9)	Ru(1c)–C(1c)	2.025(8)
Fe(2a)–C(1a)	2.048(8)	Fe(2b)–C(1b)	2.064(8)	Fe(2c)–C(1c)	2.078(9)
Fe(2a)–C(2a)	2.087(9)	Fe(2b)–C(2b)	2.099(9)	Fe(2c)–C(2c)	2.081(9)
Fe(2a)–C(3a)	2.122(8)	Fe(2b)–C(3b)	2.115(8)	Fe(2c)–C(3c)	2.114(8)
Fe(3a)–C(4a)	2.138(7)	Fe(3b)–C(4b)	2.132(7)	Fe(3c)–C(4c)	2.133(8)
Fe(3a)–C(5a)	2.125(8)	Fe(3b)–C(5b)	2.141(8)	Fe(3c)–C(5c)	2.116(9)
Fe(3a)–C(6a)	2.103(8)	Fe(3b)–C(6b)	2.122(8)	Fe(3c)–C(6c)	2.112(8)
Ru(4a)–C(5a)	2.107(9)	Ru(4b)–C(5b)	2.115(10)	Ru(4c)–C(5c)	2.094(10)
<i>Ru–C(cyclopentadienyl) distances</i>					
Ru(1a)–C(51a)	2.195(15)	Ru(1b)–C(51b)	2.211(11)	Ru(1c)–C(51c)	2.197(15)
Ru(1a)–C(52a)	2.257(12)	Ru(1b)–C(52b)	2.256(13)	Ru(1c)–C(52c)	2.233(10)
Ru(1a)–C(53a)	2.251(17)	Ru(1b)–C(53b)	2.273(14)	Ru(1c)–C(53c)	2.253(15)
Ru(1a)–C(54a)	2.244(13)	Ru(1b)–C(54b)	2.256(12)	Ru(1c)–C(54c)	2.253(12)
Ru(1a)–C(55a)	2.241(14)	Ru(1b)–C(55b)	2.258(11)	Ru(1c)–C(55c)	2.251(14)
Ru(4a)–C(61a)	2.245(13)	Ru(4b)–C(61b)	2.224(17)	Ru(4c)–C(61c)	2.270(13)
Ru(4a)–C(62a)	2.257(12)	Ru(4b)–C(62b)	2.236(14)	Ru(4c)–C(62c)	2.278(11)
Ru(4a)–C(63a)	2.237(8)	Ru(4b)–C(63b)	2.209(17)	Ru(4c)–C(63c)	2.220(10)
Ru(4a)–C(64a)	2.252(10)	Ru(4b)–C(64b)	2.201(26)	Ru(4c)–C(64c)	2.247(13)
Ru(4a)–C(65a)	2.263(9)	Ru(4b)–C(65b)	2.205(12)	Ru(4c)–C(65c)	2.236(11)
<i>Distances within $\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6$ molecule</i>					
C(1a)–C(2a)	1.425(12)	C(1b)–C(2b)	1.431(12)	C(1c)–C(2c)	1.416(12)
C(2a)–C(3a)	1.411(13)	C(2b)–C(3b)	1.426(13)	C(2c)–C(3c)	1.439(13)
C(2a)–C(4a)	1.488(13)	C(2b)–C(4b)	1.496(14)	C(2c)–C(4c)	1.486(12)
C(4a)–C(5a)	1.416(11)	C(4b)–C(5b)	1.429(12)	C(4c)–C(5c)	1.405(11)
C(5a)–C(6a)	1.424(12)	C(5b)–C(6b)	1.431(12)	C(5c)–C(6c)	1.444(13)
<i>Carbon–oxygen distances within carbonyl ligands</i>					
C(11a)–O(11a)	1.169(13)	C(11b)–O(11b)	1.128(12)	C(11c)–O(11c)	1.159(12)
C(12a)–O(12a)	1.185(14)	C(12b)–O(12b)	1.168(14)	C(12c)–O(12c)	1.167(14)
C(21a)–O(21a)	1.148(12)	C(21b)–O(21b)	1.138(12)	C(21c)–O(21c)	1.148(12)
C(22a)–O(22a)	1.147(12)	C(22b)–O(22b)	1.164(12)	C(22c)–O(22c)	1.141(13)
C(31a)–O(31a)	1.151(13)	C(31b)–O(31b)	1.152(12)	C(31c)–O(31c)	1.155(13)
C(32a)–O(32a)	1.151(13)	C(32b)–O(32b)	1.139(13)	C(32c)–O(32c)	1.157(13)
C(33a)–O(33a)	1.132(12)	C(33b)–O(33b)	1.151(13)	C(33c)–O(33c)	1.146(13)
C(41a)–O(41a)	1.146(11)	C(41b)–O(41b)	1.132(11)	C(41c)–O(41c)	1.151(12)
C(42a)–O(42a)	1.141(12)	C(42b)–O(42b)	1.139(13)	C(42c)–O(42c)	1.137(13)

Table 3 (continued)

Molecule a		Molecule b		Molecule c	
<i>Carbon-carbon distances with cyclopentadienyl ligands</i>					
C(51a)–C(52a)	1.374(28)	C(51b)–C(52b)	1.354(23)	C(51c)–C(52c)	1.372(27)
C(52a)–C(53a)	1.336(22)	C(52b)–C(53b)	1.381(18)	C(52c)–C(53c)	1.345(22)
C(53a)–C(54a)	1.359(26)	C(53b)–C(54b)	1.438(24)	C(53c)–C(54c)	1.365(22)
C(54a)–C(55a)	1.360(29)	C(54b)–C(55b)	1.356(24)	C(54c)–C(55c)	1.362(28)
C(55a)–C(51a)	1.402(23)	C(55b)–C(51b)	1.406(20)	C(55c)–C(51c)	1.392(24)
C(61a)–C(62a)	1.368(18)	C(61b)–C(62b)	1.311(24)	C(61c)–C(62c)	1.365(17)
C(62a)–C(63a)	1.382(20)	C(62b)–C(63b)	1.294(38)	C(62c)–C(63c)	1.393(20)
C(63a)–C(64a)	1.379(16)	C(63b)–C(64b)	1.359(38)	C(63c)–C(64c)	1.352(20)
C(64a)–C(65a)	1.401(16)	C(64b)–C(65b)	1.330(36)	C(64c)–C(65c)	1.390(20)
C(65a)–C(61a)	1.422(20)	C(65b)–C(61b)	1.338(29)	C(65c)–C(61c)	1.423(22)
<i>Distances within hexane of solvation</i>					
C(1S)–C(2S)	1.48(4)	C(3S)–C(4S)	1.48(4)	C(5S)–C(6S)	1.45(4)
C(2S)–C(3S)	1.16(5)	C(4S)–C(5S)	1.39(4)		

ing data, the infrared spectrum of **1** shows bands (six) in the terminal $\nu(\text{CO})$ region from 2040 to 1940 cm^{-1} and one band in the bridging $\nu(\text{CO})$ region at 1798 cm^{-1} .

A highly dissymmetric nature of molecule **1** is evidenced by the ^1H and ^{13}C NMR spectra of the ligand C_6H_6 . Six resonances are observed in each spectrum. The proton signals occur in the broad range of δ 10.48 to -0.73 , whereas the ^{13}C signals are noted between δ 177.6 and 42.7. The splitting patterns due to proton-proton coupling strongly suggest that the C_6H_6 represents a single ligand rather than, for example, two C_3H_3 ligands. The ^{13}C NMR signals at δ 61.9 and 42.7 appear as triplets with $^1J_{\text{CH}} = 162$ and 156 Hz respectively, indicating that these two CH_2 carbon atoms are sp^2 hybridized [7]. Similarly, the doublet signals at δ 177.6 and 72.4 with $^1J_{\text{CH}} = 154$ and 161 Hz respectively, implicate sp^2 hybridization at these two CH carbon atoms. The singlets at δ 110.3 and 90.3 are due to the remaining, quaternary carbon atoms. As expected, the two $\eta^5\text{-C}_5\text{H}_5$ groups are inequivalent in the ^1H and ^{13}C NMR spectra.

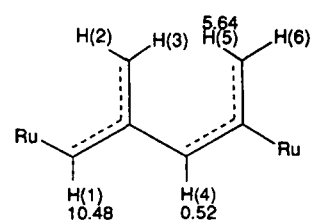
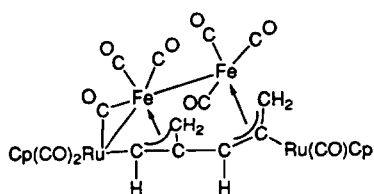
Although these spectroscopic data are helpful in the determination of some structural features of molecule **1**, complete elucidation of the structure required an X-ray diffraction analysis (vide infra). With the knowledge of structure, it is possible to assign some of the resonances in the ^1H NMR spectrum to the appropriate hydrogens of C_6H_6 . Such assignments are made possible by the relative values of J , which are either close to 1 Hz or

approximately 3 Hz. By assuming that the former are 2J between CH_2 group protons, and the latter are 4J between two syn (or syn-like) η^3 -allylic protons—the so-called W-effect [8]—resonances have been assigned to H(1), H(5) and H(6) (cf. Scheme 1). However, the remaining signals of C_6H_6 cannot be assigned unequivocally from these data.

3.2. Description of the structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2\text{Fe}_2(\text{CO})_8(\mu\text{-CO})(\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6)]_3 \cdot \text{C}_6\text{H}_{14}$

The crystal is composed of the polynuclear Ru_2Fe_2 -containing molecules and hexane of crystallization in a 3:1 ratio. All molecules lie in general positions and the crystallographic asymmetric unit consists of three molecules of the polynuclear species and one C_6H_{14} molecule. Fig. 1 provides a packing diagram. Interatomic distances appear in Table 3; the tetranuclear Ru_2Fe_2 molecules have only C_1 symmetry and are therefore chiral; the crystal is composed of an ordered racemic mixture by virtue of the crystallographic inversion centers. Fig. 2 shows the molecular geometry and atomic labelling scheme for each of the three crystallographically-independent tetranuclear molecules.

Atoms in the three Ru_2Fe_2 -containing molecules are labelled with suffixes 'a', 'b' or 'c'. In the subsequent discussion we will refer primarily to the dimensions in the 'a'-molecule, with information on the 'b' and 'c' molecules following in parentheses.



Scheme 1.

The Ru_2Fe_2 -containing molecule is not strictly a metal cluster, since it contains only a bent RuFe_2 moiety with $\text{Ru}(1a)\text{--Fe}(2a) = 2.687(1)$ Å, $\text{Fe}(2a)\text{--Fe}(3a) = 2.895(2)$ Å and $\angle\text{Ru}(1a)\text{--Fe}(2a)\text{--Fe}(3a) = 131.2(1)^\circ$ and an isolated ruthenium atom, $\text{Ru}(4a)$. (Corresponding distances and angles in the other molecules are: $\text{Ru}(1b)\text{--Fe}(2b) = 2.679(1)$ Å, $\text{Fe}(2b)\text{--Fe}(3b) = 2.871(2)$ Å and $\text{Ru}(1b)\text{--Fe}(2b)\text{--Fe}(3b) = 129.5(1)^\circ$; $\text{Ru}(1c)\text{--Fe}(2c) = 2.687(1)$ Å, $\text{Fe}(2c)\text{--Fe}(3c) = 2.906(2)$ Å and $\text{Ru}(1c)\text{--Fe}(2c)\text{--Fe}(3c) = 131.8(1)^\circ$.)

The $\text{Ru}(1a)\text{--Fe}(2a)$ linkage is bridged by the lone bridging carbonyl ligand in the structure, with $\text{Ru}(1a)\text{--C}(12a) = 2.049(10)$ Å, $\text{Fe}(2a)\text{--C}(12a) = 1.953(10)$ Å, $\angle\text{Ru}(1a)\text{--C}(12a)\text{--O}(12a) = 135.3(7)^\circ$ and $\angle\text{Fe}(2a)\text{--C}(12a)\text{--O}(12a) = 140.0(7)^\circ$; this carbonyl ligand is thus in a slightly unsymmetrical bridging location (as is almost inevitable from its association with a heteronuclear metal–metal bond). However, it is definitely not a so-called [9] ‘semi-bridging’ ligand. (Values for the other molecules are $\text{Ru}(1b)\text{--C}(12b) = 2.023(9)$ Å, $\text{Fe}(2b)\text{--C}(12b) = 1.964(11)$ Å, $\text{Ru}(1b)\text{--C}(12b)\text{--O}(12b) = 136.6(7)^\circ$, $\text{Fe}(2b)\text{--C}(12b)\text{--O}(12b) = 138.5(7)^\circ$; $\text{Ru}(1c)\text{--C}(12c) = 2.061(10)$ Å, $\text{Fe}(2c)\text{--C}(12c) = 1.968(10)$ Å, $\text{Ru}(1c)\text{--C}(12c)\text{--O}(12c) = 136.4(7)^\circ$, $\text{Fe}(2c)\text{--C}(12c)\text{--O}(12c) = 139.8(7)^\circ$.)

The remaining carbonyl ligands are all in terminal positions. Ruthenium–carbonyl bond lengths within the three independent molecules range from $\text{Ru}(1a)\text{--C}(11a) = 1.839(10)$ Å to $\text{Ru}(1b)\text{--C}(11b) = 1.879(10)$ Å, with an average value of 1.859 Å; terminal iron–carbonyl bond lengths range from $\text{Fe}(3c)\text{--C}(32c) = 1.761(11)$ Å to $\text{Fe}(2b)\text{--C}(21b) = 1.802(10)$ Å, averaging 1.782 Å.

The carbon–oxygen distance within the bridging ligand is $\text{C}(12a)\text{--O}(12a) = 1.185(14)$ Å in molecule ‘a’

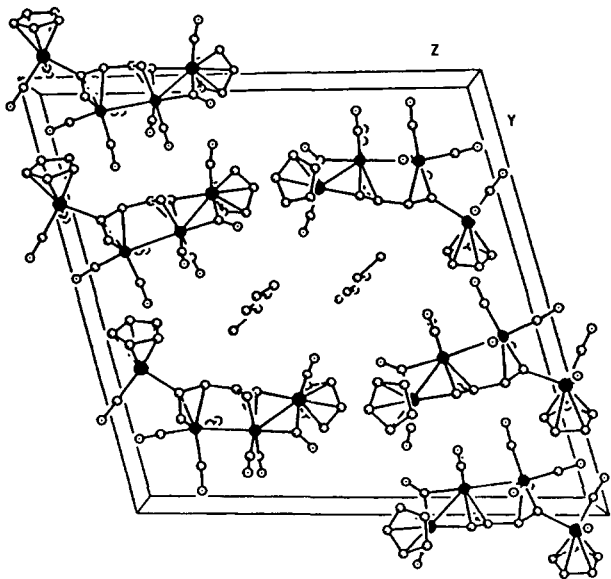


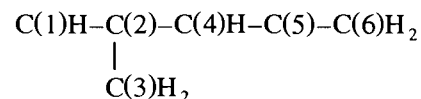
Fig. 1. Packing of molecules in the unit cell, projected on (100), for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2\text{Fe}_2(\text{CO})_8(\mu\text{-CO})(\mu_4, \eta^6\text{-C}_6\text{H}_6)]_3 \cdot \text{C}_6\text{H}_{14}$. Hydrogen atoms are omitted for clarity.

(1.168(14) Å and 1.167(14) Å respectively, in the other two molecules ‘b’ and ‘c’). The terminal C–O distances range from 1.132(12)–1.169(13) Å, averaging 1.148 Å, for molecule ‘a’ (1.128(12)–1.164(12), averaging 1.143 Å, for molecule ‘b’; 1.137(13)–1.159(12), averaging 1.149 Å, for molecule ‘c’).

The η^5 -cyclopentadienyl ligands are linked to ruthenium atoms. Atom $\text{Ru}(1a)$ is associated with $\text{Ru}\text{--C}$ distances of 2.195(15)–2.257(12), averaging 2.238 Å; atom $\text{Ru}(4a)$ (which is in a different chemical environment to $\text{Ru}(1a)$) is associated with $\text{Ru}\text{--C}$ distances of 2.237(8)–2.263(9), averaging 2.251 Å. Distances for the other molecules are as follows: $\text{Ru}(1b)\text{--C} = 2.211(11)$ –2.273(14), averaging 2.250 Å; $\text{Ru}(4b)\text{--C} = 2.201(26)$ –2.236(14), averaging 2.215 Å; $\text{Ru}(1c)\text{--C} = 2.197(15)$ –2.253(15), averaging 2.237 Å; $\text{Ru}(4c)\text{--C} = 2.220(10)$ –2.278(11), averaging 2.250 Å. It should be noted that five of the six $\eta^5\text{-C}_5\text{H}_5$ ligands are well behaved, undergoing normal thermal motion, and associated with typical C–C distances. The sixth (that defined by atoms $\text{C}(61b) \rightarrow \text{C}(65b)$) is poorly behaved, is undergoing substantial librational motion (U_{eq} values of 0.093–0.168(16) Å²) and is associated with abnormal, librationaly contracted, C–C distances of 1.294(38)–1.359(38), averaging 1.326 Å.

3.3. The $\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6$ ligand

The most interesting portion of the structure is the $\mu_4\text{-}\eta^6\text{-C}_6\text{H}_6$ ligand. This can be represented as below.



This ligand has resulted from the coupling of two allenyl groups in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$ through the carbons $\beta(\text{C}(2))$ and $\gamma(\text{C}(4))$. Coupling reactions of allenyl ligands in transition-metal complexes have been little investigated. Recently, reactions have been reported of $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mo}(\text{CO})_3]_2(\mu\text{-}\eta^2, \eta^3\text{-CHCCH}_2)^+$ with $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ [10] and of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}=\text{C}=\text{CH}_2$ with $\text{H}_2\text{Os}_3(\text{CO})_{10}$ [11]. In both cases, allenyl group coupling through the γ -carbon atoms (i.e. CH_2) has been confirmed by X-ray crystallography. In contrast to the foregoing reactions, allene oligomerization and polymerization effected by metal complexes, especially those of Ni, Pd, and Rh, are well known processes [12–14]. Both central C–central C/terminal C–terminal C and central C–terminal C bond formation has been observed.

Atom $\text{C}(1)$ is σ -bonded to $\text{Ru}(1)$ ($\text{Ru}(1a)\text{--C}(1a) = 2.037(8)$ Å, $\text{Ru}(1b)\text{--C}(1b) = 2.023(9)$ Å, $\text{Ru}(1c)\text{--C}(1c) = 2.025(8)$ Å) and atom $\text{C}(5)$ is σ -bonded to $\text{Ru}(4)$ ($\text{Ru}(4a)\text{--C}(5a) = 2.107(9)$ Å, $\text{Ru}(4b)\text{--C}(5b) = 2.115(10)$ Å, $\text{Ru}(4c)\text{--C}(5c) = 2.094(10)$ Å). The latter set of bond lengths correspond to those in a typical

($\eta^5\text{-C}_5\text{H}_5$)Ru(CO)₂(alkyl) system. The C(1)–C(2)–C(3) system forms a pseudo η^3 -allyl system with Fe(2), while the C(4)–C(5)–C(6) system forms a pseudo η^3 -allyl system with Fe(3). That the η^3 -allyl system associ-

ated with Fe(2a) involves iron–carbon distances [15] of Fe(2a)–C(1a) = 2.048(8), Fe(2a)–C(2a) = 2.087(9) and Fe(2a)–C(3a) = 2.122(8) Å (the other molecules show similar trends with values of 2.064(8), 2.099(9), 2.115(8)

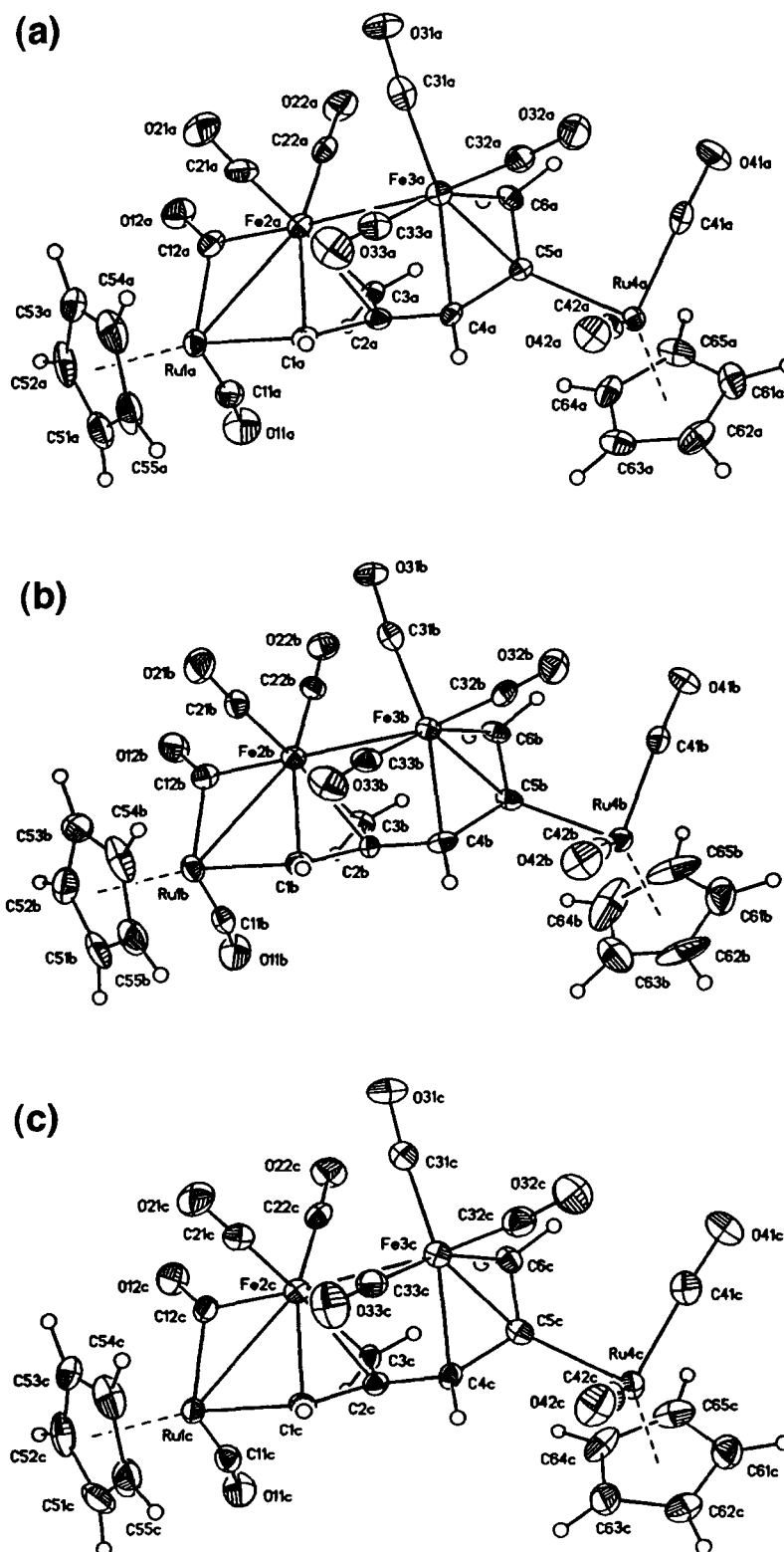


Fig. 2. Labelling of atoms and molecular geometry: (a) the 'a'-molecule; (b) the 'b'-molecule; (c) the 'c'-molecule.

Å for molecule 'b' and 2.078(9), 2.081(9), 2.114(8) Å for molecule 'c'). Carbon–carbon distances within this system are normal [16] C(1a)–C(2a) = 1.425(12) and C(2a)–C(3a) = 1.411(13) Å (1.431(12), 1.426(13) Å in molecule 'b'; 1.416(12), 1.439(13) Å in molecule 'c'). The η^3 -allyl system associated with Fe(3a) is more symmetrically bonded, with iron–carbon distances of Fe(3a)–C(4a) = 2.138(7), Fe(3a)–C(5a) = 2.125(8) and Fe(3a)–C(6a) = 2.103(8) Å (cf., 2.132(7), 2.141(8), 2.122(8) Å in molecule 'b' and 2.133(8), 2.116(9), 2.112(8) Å in molecule 'c'). Carbon–carbon distances are, again, characteristic of those in π -allyl–metal complexes [16], with C(4a)–C(5a) = 1.416(10) and C(5a)–C(6a) = 1.424(12) Å (1.429(12), 1.431(12) Å in molecule 'b'; 1.405(11), 1.444(13) Å in molecule 'c').

Finally, we note that the bond linking between the two pseudo- η^3 -allyl systems is the longest in the C₆H₆ moiety. The C(2a)–C(4a) distance of 1.488(13) Å is characteristic of a C(sp²)–C(sp²) single bond. (Values of 1.496(14) and 1.486(12) Å are found for this linkage in molecules 'b' and 'c' respectively.)

3.4. The hexane of solvation

The presence of only one hexane molecule in the asymmetric unit, along with three Ru₂Fe₂-containing molecules, confirms that the crystal is truly triclinic (rather than, say, trigonal and not recognized as such). The hexane molecule is in the characteristic completely staggered conformation and exhibits huge 'thermal displacement coefficients' (U_{eq} values of 0.305–0.584 Å²); the associated carbon–carbon distances (1.16(5)–1.48(4) Å) are subject to large systematic errors and should be taken cum grano salis.

3.5. General considerations

The molecule appears to be remarkably dissymmetric, even though each metal atom individually achieves the '18-electron configuration'. Thus, Ru(1) has an (η^5 -C₅H₅)Ru(CO)(μ -CO)(σ -C)(σ -Fe) environment, whereas Ru(4) has the much simpler (η^5 -C₅H₅)Ru(CO)₂(σ -C) arrangement. Atom Fe(2) has an Fe(CO)₂(η^3 -allyl)(μ -CO)(σ -Ru)(σ -Fe) connectivity, whereas Fe(3) has a simpler Fe(CO)₃(η^3 -allyl)(σ -Fe) connectivity.

Acknowledgements

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