

**MOLECULAR STRUCTURE AND FLUXIONAL BEHAVIOUR OF THE
 IRON-RHODIUM METHOXYMETHYLIDYNE CLUSTER COMPLEX**
 $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$

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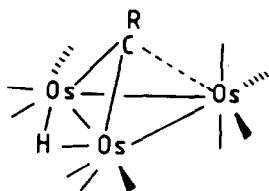
Summary

The complex $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$ prepared by treatment of $\text{Fe}_3(\mu\text{-H})(\mu\text{-COCH}_3)(\text{CO})_{10}$ with $\text{Rh}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$, has been examined by single crystal X-ray diffraction. The compound crystallises in the monoclinic space group $C2/c$ (No. 15) with a 25.409(2), b 8.129(1), c 17.044(1) Å, β 103.744(6)°, V 3419.6(6) Å³ and D_c 2.02 g cm⁻³ for $Z = 8$ and $M = 519.8$. Data were collected for $2^\circ \leq \theta \leq 30^\circ$ with graphite monochromated X-radiation (Mo- K_α) using an Enraf-Nonius CAD4-F diffractometer. The structure was refined to $R = 0.025$ ($R_w = 0.037$) for 3557 observed [$I \geq 3(\sigma I)$], absorption corrected data. The complex contains an asymmetrically bonded methoxymethylidyne ligand capping an Fe_2Rh triangular face (Fe(1)–C(8) 1.863(3), Fe(2)–C(8) 1.881(3), Rh–C(8) 2.211(3) Å). The terminal carbonyl ligand on the rhodium atom shows slight semi-bridging interactions with the two iron atoms (Fe(1)···C(7) 2.888(4), Fe(2)···C(7) 2.769(4) Å, Rh–C(7)–O(7) 169.1(4)°). The iron–iron vector is spanned by a (directly located) μ -hydride ligand. Variable temperature ¹³C NMR studies reveal fluxional behaviour, including a temperature dependence both of the alkylidyne carbon chemical shift (δ 323.5 at +80°C, δ 319.2 at –90°C) and its ¹⁰³Rh coupling constant ($^1J(\text{Rh}-\text{C})$ 23 Hz at –90°C, 26 Hz at +80°C). These data suggest an increased interaction of the ‘semi- μ_3 ’ alkylidyne ligand with the rhodium centre at higher temperatures, primarily associated with the highest energy fluxional process. Extended Hückel MO calculations on this complex allow a rationalisation of the ‘semi- μ_3 ’ nature of the COCH₃ group.

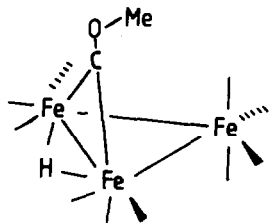
Introduction

Recent structural studies on the molecules $\text{Os}_3(\mu\text{-H})(\mu\text{-CR})(\text{CO})_{10}$ ($R = \text{H}$ (**1a**) [1], ($R = \text{Ph}$ (**1b**)) [2] and ($R = \text{CH}_2\text{CHMe}_2$ (**1c**)) [3] reveal an interesting ‘semi- μ_3 ’ alkylidyne ligand bonding mode, one where the formally electron deficient al-

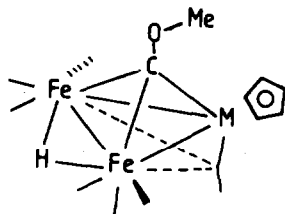
kylydyne carbon is involved in a significant interaction with the saturated 18 electron $\text{Os}(\text{CO})_4$ unit. It is proposed [1,2] that the $\text{Os}(\text{CO})_4$ fragment in these compounds acts as an electron donor towards the electrophilic alkylidyne carbon atom, a suggestion substantiated by the recent synthesis and structural determination of $\text{Os}_3(\mu\text{-H})(\mu_3\text{-CPh})(\text{CO})_9(\eta^1\text{-C}(\text{OMe})_2)$ (**2**). This complex contains the more nucleophilic carbene group $\text{C}(\text{OMe})_2$ replacing one of the carbonyls in the $\text{Os}(\text{CO})_4$ unit, and has the shortest $\text{Os}\cdots\text{C}$ contact (2.286(12) Å) yet observed in these systems [4]. In contrast, the related methylidyne cluster $\text{Fe}_4(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-CH})(\text{CO})_{12}$ [5], with an 'agostic' [6] CH unit, appears to involve the C-H bond in a donor interaction towards one of the $\text{Fe}(\text{CO})_3$ moieties [5,7].



(1)



(3a)



(4, M = CO)

5, M = Rh)

In complexes **1a-1c** and **2** the dihedral angle between the Os_3 and $\overline{\text{Os}(\mu\text{-C})\text{Os}}$ planes is acute, ranging from 66.6° for **2** [4] to 82.1° for **1c** [3]. However for the related methoxy-substituted alkylidyne complexes $\text{M}_3(\mu\text{-H})(\mu\text{-COCH}_3)(\text{CO})_{10}$ (M = Fe (**3a**)) [8], (M = Ru (**3b**)) [9] and (M = Os (**3c**)) [10] there is a less significant 'semi- μ_3 ' character, with angles between the M_3 and $\overline{\text{M}(\mu\text{-C})\text{M}}$ planes of 91.1° for **3a** [8] and 94.9° for **3b** [9a]. It has been suggested that the differing 'semi- μ_3 ' character in these nominally rather similar alkylidyne complexes arises from the π donor ability of the methoxy substituent, which reduces the electrophilicity of the alkylidyne carbon, and thus alleviates the driving force for interaction with the electron-rich $\text{Os}(\text{CO})_4$ centre [1]. Other bridged triosmium complexes of the type

$\text{Os}_3(\mu\text{-H})(\mu\text{-X})(\text{CO})_{10}$ have the $\mu\text{-X}$ substituent *exo* to the Os_3 triangle, with the interplanar angle between Os_3 and $\overline{\text{Os}(\mu\text{-X})\text{Os}}$ invariably obtuse [11]. In $\text{Os}_3(\mu\text{-H})(\mu\text{-CH.CH=NEt}_2)(\text{CO})_{10}$ for example this angle is 106° [12].

We have recently reported [13] the reaction of **3a** with $\text{Co}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ resulting in $\text{CoFe}_2(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$ (**4**) whereby the d^8 ML_4 $\text{Fe}(\text{CO})_4$ unit in **3a** has been replaced by the isolobal [14] fragment $\text{Co}(\text{CO})(\eta\text{-C}_5\text{H}_5)$. This complex contains an asymmetrically bonded methoxymethylidyne ligand involved in a weaker interaction with the cobalt than with the two iron atoms. ^{13}C NMR studies revealed fluxional behaviour, with the alkylidyne carbon resonance moving to high field at lower temperatures. This interesting temperature dependence has also been reported for the osmium compounds **1b** and **1c** [2,3] and attributed to conformational equilibria involving the alkylidyne ligand in varying degrees of interaction with the d^8 ML_4 unit [2,3,13]. In an effort to shed further light on these solution processes, the rhodium analogue of complex **4** has been synthesised and the molecular structure and fluxional behaviour investigated in the hope that the presence of ^{103}Rh coupling to the alkylidyne carbon would be informative. These results are now discussed.

Experimental

$\text{Fe}_3(\mu\text{-H})(\mu\text{-COCH}_3)(\text{CO})_{10}$ [13] and $\text{Rh}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [57] were prepared as reported previously. Reactions were performed under an oxygen-free dinitrogen atmosphere using standard Schlenk tube techniques. Solvents were freshly distilled prior to use; light petroleum refers to that fraction b.p. $40\text{--}60^\circ\text{C}$. ^1H and ^{13}C NMR measurements were obtained on a Bruker WP 200SY instrument. Infra-red spectra were obtained on a Perkin-Elmer 983, and high resolution mass spectra on a Kratos 902S instrument.

*Preparation of $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$ (**5**)*

$\text{Fe}_3(\mu\text{-H})(\mu\text{-COCH}_3)(\text{CO})_{10}$ 1.97 g (4 mmol) and $\text{Rh}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ 1.0 g (4.46 mmol) in 60 cm^3 light petroleum were refluxed under vacuum for 12 h at 90°C . There was little colour change in the purple solution. Removal of solvent in vacuo and chromatography on a column of Florisil (100–200 mesh) using light petroleum/ CH_2Cl_2 mixtures as eluant afforded the following bands in order of elution (a) yellow- $\text{Fe}(\text{CO})_5$ (IR), (b) pink unreacted $\text{Fe}_3(\mu\text{-H})(\mu\text{-COCH}_3)(\text{CO})_{10}$ (trace), (c) orange unreacted $\text{Rh}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ (IR), (d) purple-red (main band), and (e) dark brown (trace-unidentified). Recrystallisation of band (d) from light petroleum afforded black crystals of the product $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$ 1.34 g (65%).

Found: C, 32.45; H, 1.55. $\text{C}_{14}\text{H}_9\text{Fe}_2\text{O}_8\text{Rh}$ calcd.: C, 32.35; H, 1.74%. Mass spectrum m/z 519.8045 (0.3 mmu deviation from $^{12}\text{C}_{14}\text{ }^1\text{H}_9\text{ }^{16}\text{O}_8\text{ }^{103}\text{Rh}\text{ }^{56}\text{Fe}_2$). IR (ν (CO) max cm^{-1} , hexane) 2070s, 2040vs, 2006vs, 1994w, 1983s, 1971m; (ν max cm^{-1} , KBr disc, selected bands) 3122w, 3023vw, 3000vw, 2950w, 2845vw, 1440m, 1222s. NMR (^1H , CDCl_3 , ambient) δ 5.43 (d, 5H, C_5H_5 , $^2J(\text{Rh-H})$ 0.7 Hz), 4.38 (s, 3H, CH_3), -19.62 (s, 1H, $\text{Fe}(\mu\text{-H})\text{Fe}$); ($^{13}\text{C}\{^1\text{H}\}$, $\text{CD}_3\text{C}_6\text{D}_5$, $+80^\circ\text{C}$) δ 323.5 (d, 1C, COCH_3 , $J(\text{Rh-C})$ 26 Hz) 209.7 (s, br, 7C, CO) 93.1 (d, 5C, C_5H_5 , $J(\text{Rh-C})$ 4 Hz) 68.8 (s, 1C, OCH_3); ($^{13}\text{C}\{^1\text{H}\}$, $\text{CD}_3\text{C}_6\text{D}_5$, -90°C) δ 319.2 (d, 1C, COCH_3 , $J(\text{Rh-C})$ 23 Hz), 212.8 (s, 2C, FeCO), 210.9 (s, 2C, FeCO), 206.2 (s, 2C, FeCO), 195.5 (d, 1C, RhCO , $J(\text{Rh-C})$ 73 Hz) 92.6 (s, br, 5C, C_5H_5), 68.2 (s, 1C, OCH_3).

X-ray crystal structure of complex 5

Crystals of **5** grow as black prisms from light petroleum. One crystal ca. $0.2 \times 0.3 \times 0.55$ mm was glued to a glass fibre and mounted in a general position on an Enraf–Nonius CAD4-F diffractometer. Unit cell dimensions were determined from a least-squares fit to the setting angles of 25 reflections, each of which was measured in four equivalent orientations. Systematic absences indicated the space group $C2/c$ (C_{2h}^6 , No. 15). A unique quadrant of data (h , 0 to 35, k , 0 to 11, l , -24 to $+24$) in the range $2 \leq \theta \leq 30^\circ$ were collected in the $\theta/2\theta$ scan mode. The reflections $5\ 5\ \bar{1}$, $0\ \bar{2}\ \bar{1}0$, and $8\ 4\ \bar{6}$ were chosen as intensity standards and measured every 2 h during data collection. Substantial decay in intensities was observed (ca. 26% over 81.5 h data collection), and corrected for. A total of 5409 data were measured yielding 4973 independent reflections. Data were corrected for Lorentz/polarisation effects, and for absorption using the method of Stuart and Walker [15]. 3557 data with $I \geq 3\sigma(I)$ were deemed observable and used in structure solution and refinement.

Solution and refinement of structure

The metal atom positions were determined using the direct methods program MITHRIL [16], remaining non-hydrogen atoms positional parameters were obtained from subsequent difference Fourier syntheses and full-matrix least-squares refinement. The bridging hydride ligand H(1) was clearly visible in a difference Fourier synthesis, as the strongest remaining feature (height $0.53\ e\ \text{\AA}^{-3}$) after inclusion of other hydrogen atoms in calculated positions (C_5H_5 C–H 1.084 Å; CH_3 C–H 1.073 Å). Free refinement of this atom led to unreasonably short Fe–H distances, and consequently a fixed calculated position, determined using the program HYDEX [17], was used with Fe–H distances ca. 1.69 Å [18]. All non-hydrogen atoms were refined with anisotropic thermal parameters, whilst the methyl and cyclopentadienyl hydrogen atoms had fixed U_{iso} values of $0.08\ \text{\AA}^2$. H(1), the hydrido ligand, was allowed free isotropic thermal motion.

Final discrepancy values R , R_w were 0.025, 0.037 respectively where $R = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$; $R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w|F_0|^2]^{1/2}$.

The function minimised during full-matrix least-squares was $\Sigma w(|F_0| - |F_c|)^2$ with the weighting function $w = 1/\sigma^2(F)$ used and judged satisfactory. The maximum shift/error in the final cycle was 0.167 [for U_{23} of C(10)], with a mean value of 0.036. The e.s.d. of an observation of unit weight, S , was 1.66 for the observed data where $S = [\Sigma(w(|F_0| - |F_c|)^2 / (N_0 - N_v))]^{1/2}$; N_0 = no. of observations. N_v = no. of variables.

A final difference Fourier synthesis showed no peaks > 0.41 or $< -0.56\ e\ \text{\AA}^{-3}$. Scattering factors were taken from ref. 19, with corrections applied for anomalous dispersion. All calculations were carried out on a Gould-SEL 32/27 mini computer using the GX suite of programs [20].

Tables of thermal parameters and structure factors are available from the author.

Crystal data. $C_{14}H_9O_8Fe_2Rh$, $M = 519.8$, monoclinic, space group $C2/c$, a 25.409(2), b 8.129(1), c 17.044(1) Å, β 103.744(6)°, V 3419.6(6) Å³, $Z = 8$, D_c 2.02 g cm⁻³, $F(000) = 2032$, Mo- K_α X-radiation, graphite monochromator, λ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 26.52 cm⁻¹.

EHMO calculations. Calculations were carried out using the programs ICON8 and FMO [21] with the extended Hückel methodology [22,23]. Orbital exponents

and H_{ii} 's for Fe [24] and Rh [25] were obtained from previous work. Interatomic distances and angles were taken from the crystal structure, with the cluster fragment idealised to C_3 symmetry and with all carbonyl C–O 1.13, Fe–C(carbonyl) 1.77 Å.

Results and discussion

Treatment of $\text{Fe}_3(\mu\text{-H})(\mu\text{-COCH}_3)(\text{CO})_{10}$ with $\text{Rh}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ in toluene at 90°C for 12 h results in high yields of the complex $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$ (**5**). The cobalt analogue, complex **4**, has been synthesised in an identical fashion [13]. The reaction involves the replacement of the d^8 ML_4 fragment $\text{Fe}(\text{CO})_4$ in the triiron precursor by the isolobal unit $\text{Rh}(\text{CO})(\eta\text{-C}_5\text{H}_5)$, with concomitant formation of $\text{Fe}(\text{CO})_5$.

High resolution mass spectral, analytical, and NMR spectroscopic data were in agreement with the above formulation. A hexane solution IR spectrum of **5** showed six bands in the region 2070–1971 cm^{-1} , virtually superimposable on the spectrum of complex **4**, except that the low frequency band at 1913 cm^{-1} observed for **4** is absent in the spectrum of **5**. This latter broad band was attributed [13] to the stretching mode of the semibridging carbonyl ligand on the cobalt atom, and its absence in **5** suggests either that it is to higher frequency * and hence hidden under the envelope of bands between 2070 and 1971 cm^{-1} , or else it is too weak and broad to be observed. An X-ray diffraction study was carried out to clarify these discrepancies.

The molecular structure of complex **5** is shown in Fig. 1, with a stereoview in Fig. 2, whilst the results of the analysis are summarised in Tables 1 and 2.

The overall disposition of the ligands about the Fe_2Rh triangle is very similar to that observed in the cobalt analogue **4**, although the two compounds are not crystallographically iso-structural.

The Fe–Fe vector is spanned by a μ -hydride ligand, with the two $\text{Fe}(\text{CO})_3$ units eclipsed to each other. The diiron–rhodium triangle is asymmetrically capped by a methoxymethylidyne group, with the Rh–C(8) distance of 2.211(3) Å noticeably longer than the Fe(1)–C(8) Fe(2)–C(8) separations of 1.863(2), 1.881(3) Å respectively. These values may be compared with the corresponding internuclear Fe–C, Rh–C distances of 2.029(6), 2.035(6) Å respectively, found in the related cluster complex $\text{RhFeW}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_9\text{H}_7)$, where a RhFeW triangle is capped by a symmetric μ_3 -tolylidyne ligand [27]. By comparison the corresponding distances in the cobalt analogue of **5** are Fe–C, 1.871(4) and 1.877(4) Å; Co–C 2.001(4) Å [13]. In addition the terminal carbonyl ligand on rhodium C(7)–O(7) appears less semibridging in the rhodium complex [Fe(1) \cdots C(7) 2.888(4), Fe(2) \cdots C(7), 2.769(4) Å, Rh–C–O 169.1(4)°, α values ** 0.57, 0.50] than in the cobalt species [Fe \cdots C 2.559(4), 2.629(4) Å, Co–C–O 164.4(4)°, α values 0.47, 0.51].

* A slightly higher (ca. 20 cm^{-1}) $\nu(\text{CO})$ stretch may be envisaged for the Rh–CO in view of the values observed for $\text{M}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$: M = Co, $\nu(\text{CO}) = 2030, 1970 \text{ cm}^{-1}$ [26]; M = Rh, $\nu(\text{CO}) 2051, 1987 \text{ cm}^{-1}$ [57].

** Semi-bridging carbonyls have an α value between 0.1 and 0.6. For a definition of the α parameter see ref 28.

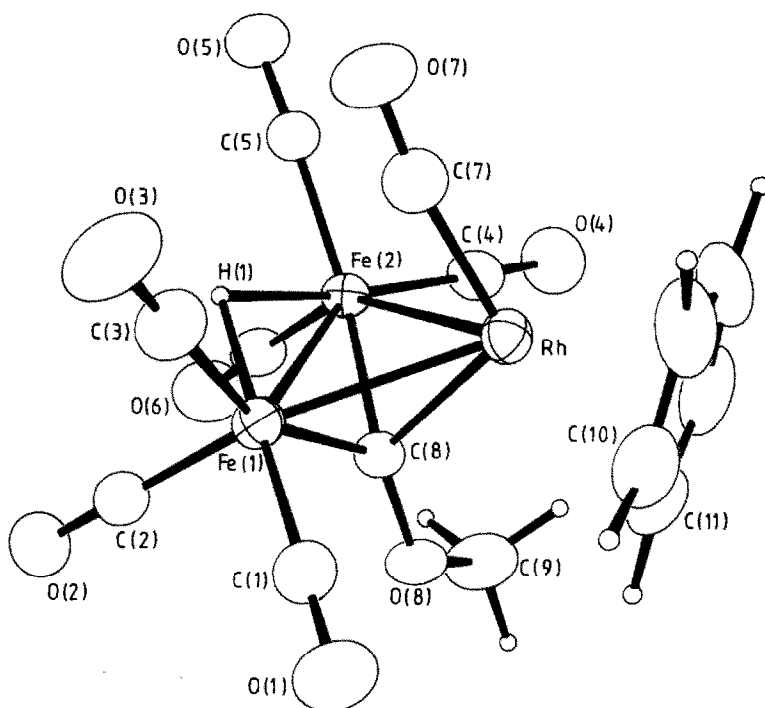


Fig. 1. The molecular structure of the complex $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$.

Taken at face value these data indicate a relatively weaker 'semi- μ_3 ' interaction in the rhodium case. Due to the differing atomic radii of cobalt and rhodium (e.g. Co 1.24, Rh 1.36 Å from unbridged M–M distances in $\text{Co}_4(\text{CO})_{12}$ [29], $\text{Rh}_4(\text{CO})_{12}$ [30]), it is not prudent to draw too detailed a conclusion from these disparate distances. Perhaps more useful criteria for distinguishing the relative extent of

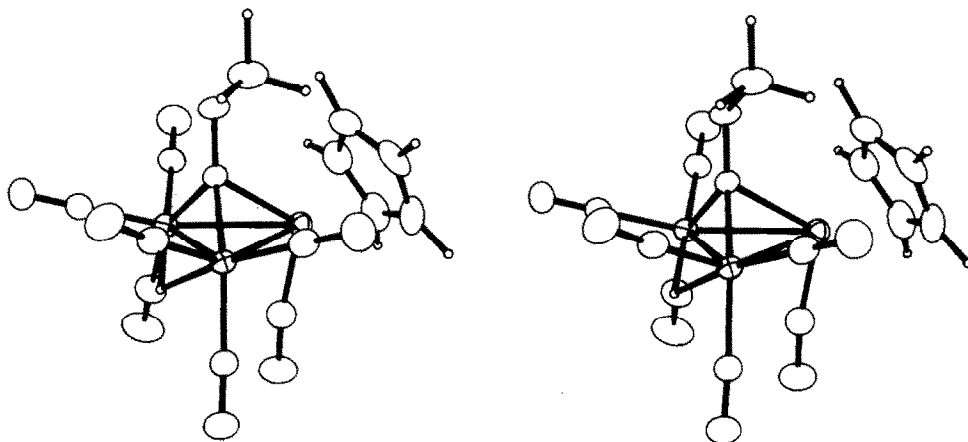


Fig. 2. Stereoscopic view of the complex $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$.

TABLE 1

ATOMIC POSITIONAL (FRACTIONAL COORDINATE) PARAMETERS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$ (U_{eq} (\AA^2) in the form $\frac{1}{3}\sum_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$)

Atom	x	y	z	U_{eq}
Rh	0.66975(1)	0.05610(3)	0.65224(1)	0.040
Fe(1)	0.57074(2)	-0.03045(4)	0.65752(3)	0.037
Fe(2)	0.60377(2)	0.26827(4)	0.69846(2)	0.034
C(1)	0.56776(14)	-0.16877(36)	0.57587(20)	0.047
C(2)	0.49949(14)	-0.00442(39)	0.63898(19)	0.047
C(3)	0.58161(16)	-0.18455(39)	0.73720(23)	0.058
C(4)	0.64588(14)	0.42432(38)	0.67455(20)	0.049
C(5)	0.62176(13)	0.30539(38)	0.80804(19)	0.045
C(6)	0.54291(14)	0.38450(39)	0.67600(19)	0.048
C(7)	0.67709(15)	0.02231(45)	0.76117(23)	0.058
C(8)	0.58716(11)	0.15058(31)	0.60065(16)	0.036
C(9)	0.57886(18)	0.34462(45)	0.49237(22)	0.065
C(10)	0.69893(19)	-0.10879(55)	0.56586(30)	0.077
C(11)	0.68454(19)	0.04382(72)	0.52797(25)	0.081
C(12)	0.7195(2)	0.1658(6)	0.5717(3)	0.081
C(13)	0.75424(17)	0.08486(63)	0.63746(33)	0.081
C(14)	0.74048(18)	-0.08361(59)	0.63292(34)	0.083
O(1)	0.56473(13)	-0.25587(31)	0.52301(18)	0.071
O(2)	0.45431(11)	0.01877(39)	0.62658(17)	0.068
O(3)	0.58934(16)	-0.28286(33)	0.78729(19)	0.087
O(4)	0.67287(12)	0.52710(35)	0.66083(18)	0.075
O(5)	0.63002(11)	0.33311(39)	0.87436(15)	0.070
O(6)	0.50342(12)	0.45654(37)	0.65796(19)	0.076
O(7)	0.68929(13)	-0.00993(43)	0.82817(16)	0.079
O(8)	0.57022(9)	0.18388(25)	0.52345(12)	0.045
H(1)	0.57318	0.10729	0.73216	0.09(1)
H(10)	0.68041	-0.22626	0.54563	0.080
H(11)	0.65229	0.06470	0.47454	0.080
H(12)	0.71959	0.29578	0.55750	0.080
H(13)	0.78588	0.14211	0.68331	0.080
H(14)	0.75953	-0.17767	0.67532	0.080
H(9A)	0.56500	0.37186	0.42922	0.080
H(9B)	0.62178	0.36559	0.50792	0.080
H(9C)	0.55976	0.43180	0.52394	0.080

interaction of the methoxymethylidene and lone carbonyl ligands with the trimetal cluster are given by the angles ϕ , ψ and θ . The values of these parameters for **5** and

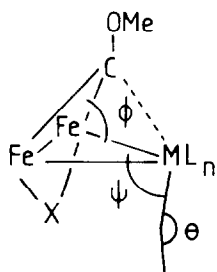


TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$

Fe(1)–Fe(2)	2.610(1)	Fe(2)–C(4)	1.768(4)
Fe(1)–Rh	2.634(1)	Fe(2)–C(5)	1.839(4)
Fe(2)–Rh	2.652(1)	Fe(2)–C(6)	1.775(4)
Fe(1)–C(8)	1.863(3)	Rh–C(7)	1.842(4)
Fe(2)–C(8)	1.881(3)	C(7)–O(7)	1.140(5)
Rh–C(8)	2.211(3)	C(9)–O(8)	1.446(5)
C(8)–O(8)	1.312(4)	Fe carbonyl C–O mean	1.137 [2]
Fe(1)···C(7)	2.888(4)	Cp C–C mean	1.405 [3]
Fe(2)···C(7)	2.769(4)	Rh–C _{Cp} mean	2.238 [2]
Fe(1)–C(1)	1.777(4)		
Fe(1)–C(2)	1.775(4)		
Fe(1)–C(3)	1.820(4)		
Fe(2)–Fe(1)–Rh	60.8(1)	Rh–C(7)–O(7)	169.1(4)
Fe(1)–Fe(2)–Rh	60.1(1)	Fe(1)–C(1)–O(1)	178.5(4)
Fe(1)–Rh–Fe(2)	59.2(1)	Fe(1)–C(2)–O(2)	177.2(4)
Fe(1)–C(8)–Fe(2)	88.4(2)	Fe(1)–C(3)–O(3)	178.8(4)
Fe(1)–C(8)–Rh	80.1(1)	Fe(2)–C(4)–O(4)	178.2(4)
Fe(2)–C(8)–Rh	80.3(1)	Fe(2)–C(5)–O(5)	176.0(3)
C(8)–O(8)–C(9)	120.8(3)	Fe(2)–C(6)–O(6)	176.8(4)
Fe(1)–C(8)–O(8)	128.6(2)		
Fe(2)–C(8)–O(8)	137.3(2)		
Rh–C(8)–O(8)	121.7(2)		

other related species are given in Table 3. Irrespective of the size of the M atom, the interplanar angle ϕ between the metal triangle and $\text{Fe}(\mu\text{-C})\text{Fe}$ unit, should decrease with increasing μ_3 character, whilst a compensatory movement of the lone carbonyl ligand across the triangular face will result in a decrease in ψ , the angle between the metal triangle and M–C vector. Such compensatory “motion”, alleviating electronic imbalance within the molecule is commonly seen in pairs of bridging carbonyl ligands [31], and has been previously discussed [13]. Coupled with this “motion” is a deviation of the M–C–O angle θ from linearity, as the carbonyl ligand moves from a terminal to a μ_3 environment. The values in Table 3 clearly show a marginally weaker interaction of the COCH_3 group with the Rh atom in **5** than is the case with the Co atom in **4**.

This may partially be associated with the general expansion of the cluster due to the incorporation of the larger rhodium atom. Whilst the Fe(1)–Rh, Fe(2)–Rh separations in **5**, 2.634(1), 2.652(1) Å respectively are unsurprisingly greater by ca.

TABLE 3

VALUES OF ϕ , ψ AND θ FOR **5** AND OTHER RELATED SPECIES (°)

ML_n	X	ϕ	ψ	θ	Ref.
$\text{Fe}(\text{CO})_3$	H	91.1	76	173	8
$\text{Rh}(\eta\text{-C}_5\text{H}_5)$ (5)	H	69.2	73.1	169.1(4)	This work
$\text{Co}(\eta\text{-C}_5\text{H}_5)$	H	64.7	69.2	164.4(4)	13
$\text{Co}(\eta\text{-C}_5\text{H}_5)$	AuPPh_3	63.3	58.9	149.9(5)	13

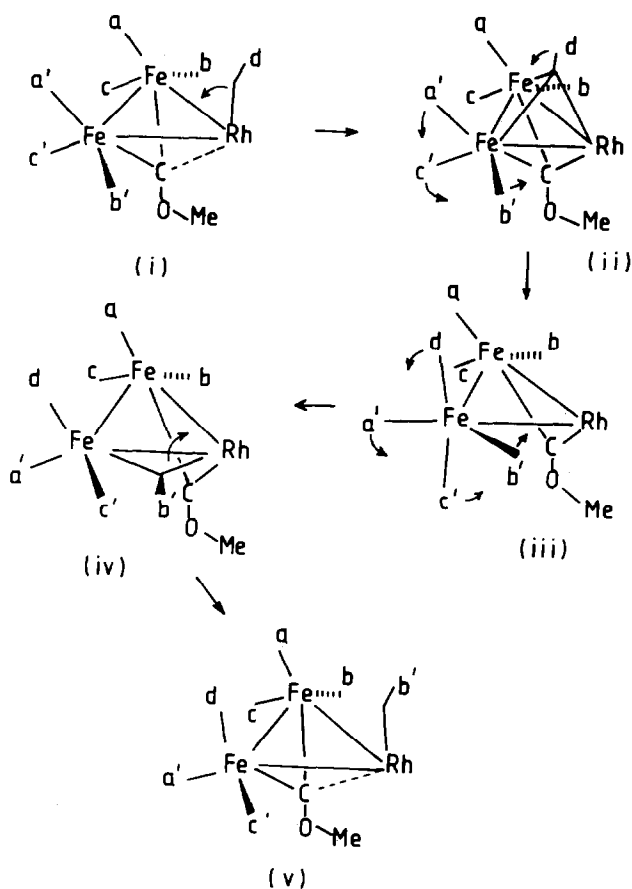
0.12 Å than the Fe–Co distances found in **4**, the Fe(1)–Fe(2) vector is also slightly but significantly increased (2.610(1) vs. 2.594(1) Å). Nevertheless these distances are normal [32], and may be compared with the Fe–Rh vectors in (CO bridged) RhFeW(μ_3 -CC₆H₄Me-4)(μ -CO)(CO)₅(η -C₅H₅)(η -C₉H₇) 2.583(1) Å [27], and in [RhFe₃(μ_4 -C)(CO)₁₂]⁻ 2.630(2) Å [33].

Other structural features of complex **5** are similar to those in related molecules. Thus the strong *trans* effect of the methoxymethylidyne ligand [9,34,35] manifests itself in the significantly longer Fe–carbonyl bonds *trans* to this ligand, viz. Fe(1)–C(3), Fe(2)–C(5) are 1.820(4), 1.839(4) Å respectively, whilst remaining Fe–carbonyl bonds range from 1.768(4)–1.777(4) Å. The COCH₃ ligand has the usual geometry with C(8)–O(8)–C(9) 120.8(3)° and the C(8)–O(8) distance of 1.312(4) Å indicative of substantial multiple bond character. The COCH₃ group asymmetrically bridges the Fe–Fe bond c.f. Fe(1)–C(8), Fe(2)–C(8) 1.863(3), 1.881(3) Å, Fe(1)–C(8)–O(8) 128.6(2), Fe(2)–C(8)–O(8) 137.3(2)°. This minor asymmetry probably arises from the disposition of the methyl group.

The C(8)–O(8)–C(9) plane is inclined at an angle of 3.2° to the Fe₂Rh triangle, and is nearly parallel with the Fe(1)–Fe(2) vector (angle between plane and line 4.8°). This latter orientation of the μ -COCH₃ group, where the plane of the ligand is essentially parallel to the bridged interatomic vector, is observed in all the structurally characterised complexes containing μ_2 -COCH₃ ligands cf. M₃(μ -H)(μ -COCH₃)(CO)₁₀ M = Fe [8], M = Ru [9] and the related triphenylphosphine aurio derivatives M₃(μ -AuPPh₃)(μ -COCH₃)(CO)₁₀ M = Ru [34], M = Os [36]. In the recently reported complex Fe₂(μ -COEt)(μ - η^2 -PhC≡CMe)(CO)₆, containing a μ -ethoxymethylidyne ligand, the Fe(μ -COC_a)Fe unit is nearly coplanar [37], whilst the *S*-alkylated CS group in [Fe₂(μ -CSEt)(CO)₃(η -C₅H₅)₂]⁺ appears to have a similar geometry [38].

NMR data are consistent with the solid state structure, though fluxional behaviour is evident. The ¹H NMR spectrum shows the expected signals in the region δ 5.43, 4.38 and -19.62 (5/3/1) due to the C₅H₅, OCH₃ and Fe(μ -H)Fe protons respectively. A ¹³C{¹H} NMR spectrum at -90°C (Fig. 3) shows a doublet resonance (*J*(Rh–C) 23 Hz) at δ 319.2 due to the alkylidyne carbon, whilst in the carbonyl region there are four signals in the ratio 2/2/2/1 at δ 212.8, 210.9, 206.2 and 195.5. The latter signal with ¹⁰³Rh coupling (*J*(Rh–C) 73 Hz) is ascribed to the carbonyl bonded to Rh (d). From previous work on Fe₃(μ -H)(μ -COCH₃)(CO)₁₀ (**3a**) [10] the other 3 signals may be assigned as follows. The resonance of δ 212.8 is ascribed to the CO groups *aa'* *trans* to μ -COCH₃, that at δ 210.9 to *bb'* *trans* to the hydride, with the signal at δ 206.2 due to *cc'* *trans* to the Fe–Rh bond. The respective signals in **3a** are at δ 212.7, 210.2 and 204.1, with the greatest discrepancy observed for the high field signals as expected, since these arise from a CO group *trans* to an Fe–Fe bond in **3a** but *trans* to a Rh–Fe bond in **5**. Similar conclusions about the relative ordering of carbonyl chemical shifts within the Os(CO)₃(μ -H)(μ -CPh)Os(CO)₃ unit in **1b** were reached using a ¹³CO enriched sample [2].

It is clear that at -90°C a fluxional process occurs resulting in pseudo-mirror symmetry and rendering the pairs of CO's *aa'*, *bb'*, and *cc'* equivalent. Either rotation of the OCH₃ group or inversion at oxygen are possibilities [10]. At +25°C a second fluxional process is evident, rendering all six carbonyls on Fe equivalent. This presumably occurs by rotation of the Fe(CO)₃ groups about their threefold axis. Such fluxional behaviour is common in cluster complexes [39] and is seen as a



SCHEME 1

high energy process in **3a** [10]. On further raising the temperature to $+80^{\circ}\text{C}$ a single broad signal for all the carbonyl ligands is seen at δ 209.7, implying a third fluxional process interchanging all the carbonyl environments.

As previously observed [13], the methylidyne signal is temperature dependent, changing smoothly from δ 319.2 at -90°C to δ 323.5 at $+80^{\circ}\text{C}$ (other resonances shift by ca. 1 ppm or less). In addition the ^{103}Rh coupling constant rises from 23 Hz at -90°C to 26 Hz at $+25^{\circ}\text{C}$. This latter rise is not a smooth one; between -90 and $+25^{\circ}\text{C}$ the measured coupling constant changes from 22.7 to 23.4 Hz (not experimentally significant) with the major increase occurring between $+25$ and $+80^{\circ}\text{C}$. It is thus tempting to link this rise with the third fluxional process equilibrating all carbonyl ligands, since this occurs above $+25^{\circ}\text{C}$.

This latter process is likely to involve an intermediate with a triply bridged CO group (and presumably a symmetric $\mu_3\text{-COCH}_3$ ligand). Scheme 1 shows the proposed mechanism. The hydride ligand is apparently not involved in any fluxional process since the resonance at δ -19.62 ($+25^{\circ}\text{C}$) is essentially unshifted in the range -90 to $+100^{\circ}\text{C}$, remaining a sharp singlet throughout with no evidence of ^{103}Rh coupling. Intermediate (iii) structurally resembles **3a**, known to undergo

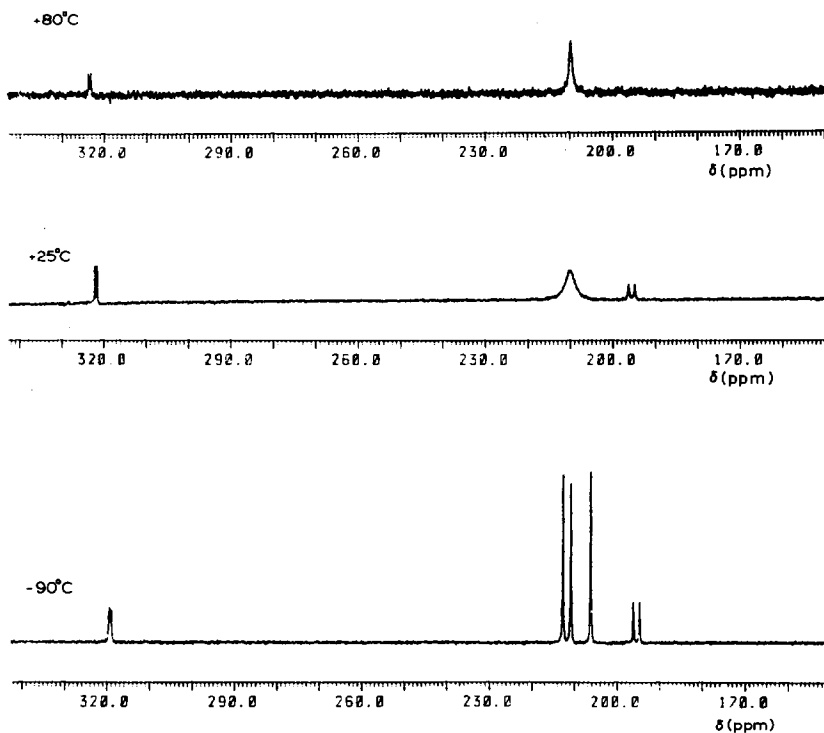


Fig. 3. Variable temperature ^{13}C (^1H) NMR spectrum of $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$ in the region 150–340 ppm.

polytopal rearrangement of the $\text{Fe}(\text{CO})_4$ unit [10], whilst (iii) and (iv) have the COCH_3 ligand in a μ_2 environment. A more deshielded ^{13}C NMR resonance is expected for a μ_2 vs. μ_3 alkyldiene carbon [13,40,41]. Passage through these intermediates may then account for the averaged downfield shift at higher temperatures.

The proposed intermediates all involve the COCH_3 ligand in stronger interactions with the Rh centre. Intuitively a greater $^1J(\text{Rh}-\text{C})$ value with decreasing Rh–C distances might be expected, and indeed Heaton et al. [42] have reported a smooth variation of $^1J(\text{Rh}-\text{C})$ with Rh–C bond lengths in the carbonyl anion $[\text{NiRh}_6(\text{CO})_{16}]^{2-}$. The limited data available for alkyldiene compounds suggests a similar correlation cf. $^1J(\text{Rh}-\text{C})$ 22 Hz, Rh–C 2.048(14) Å in $\text{RhW}(\mu\text{-CC}_6\text{H}_4\text{Me}_4)(\text{CO})_2(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_9\text{H}_7)$ [43]; and $^1J(\text{Rh}-\text{C})$ 38 Hz, Rh–C (av.) 1.962(9) Å in $[\text{Rh}_3(\mu_3\text{-CH})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_3]^+$ [44]. The complex $\text{Rh}_2\text{W}(\mu_3\text{-CMe})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2$ has intermediate values viz. $^1J(\text{Rh}-\text{C})$ 30 Hz, Rh–C 2.026(7) Å [45]. In view of these empirical values it is not too unreasonable to postulate an averaged closer Rh–C alkyldiene contact at elevated temperatures. The above data also suggests the temperature dependence of the alkyldiene ^{13}C shift may be due to the involvement of this ligand in a fluxional process affecting the molecule as a whole, rather than some unspecified conformational equilibria as previously suggested [13]. Inspection of the thermal ellipsoid of C(8) (Fig. 1) suggests this atom is

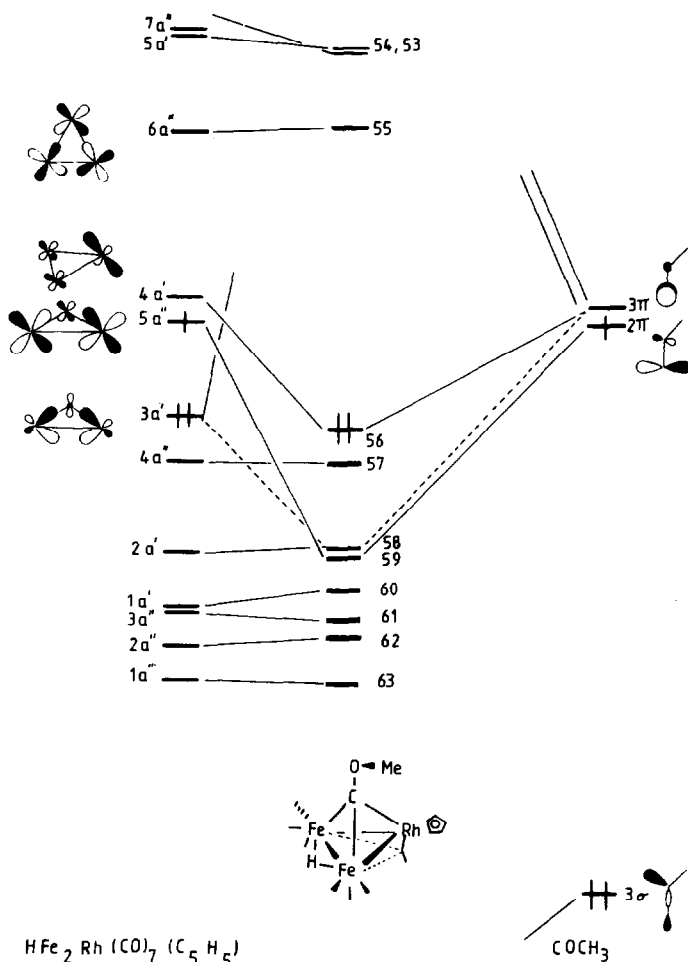


Fig. 4. Orbital interaction diagram between the fragments COCH_3 and $\text{Fe}_2\text{Rh}(\mu\text{-H})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$.

rigidly held and it shows no significant anisotropy. This is consistent with little free vibration toward the Rh centre.

In order to enhance our understanding of the interaction between the COCH_3 ligand and the cluster framework, EHMO calculations were carried out on $\text{Fe}_2\text{Rh}(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$ analysing this molecule in terms of the fragments COCH_3 and $\text{Fe}_2\text{Rh}(\mu\text{-H})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$. The electron partitioning shown in the interaction diagram (Fig. 4) emphasises the formal 3 electron donor nature of COCH_3 as an alkoxyalkylidyne ligand, whilst a more realistic partitioning as COCH_3^+ reveals its similarity to a methylated carbonyl ligand [8]. Indeed there are close analogies between the orbitals of COCH_3 and those of both CO and CR (R = alkyl, aryl). The bonding interactions of the latter ligand with trinuclear transition metal clusters are well understood, and have been examined in some detail by various MO and PES studies [24,46–49].

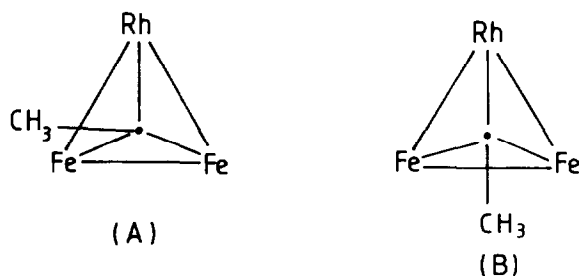
In line with previous studies we find that there are four orbitals of the COCH_3 fragment which interact well, and provide most of the bonding with the cluster

fragment. These are the 1σ at ca. -19.9 eV (not shown) and the three frontier orbitals, the 3σ , 2π and 3π (corresponding to the 5σ and π^* orbitals of CO, and the sp hybrid and degenerate p orbitals of the axially symmetric CR fragment [24]). The 'bent' disposition of the methyl group raises the degeneracy of the π orbitals, producing a separation of ca. 0.14 eV between 2π and 3π . This is rather smaller than the corresponding gaps calculated for the related non-axially symmetric CR ligands; CNEt₂, 6.1 eV from Kostić and Fenske's study [50], ca. 1.5 eV by Schubert et al. [51]; and CPh ca. 1 eV [52]. The 3σ is suitably hybridised to act as a σ donor to the cluster, and also constitutes the "lone pair" on the oxygen atom.

The general features of the interaction diagram are similar to those of the Hoffmann and Schilling study on Co₃(μ_3 -CH)(CO)₉ [24]. Thus we find three frontier orbitals, $3a'$, $5a''$, and $4a'$ of the cluster fragment interact well with the COCH₃ ligand. $3a'$ is localised on the two iron atoms and is primarily composed of an in-phase combination of d_{xz} , with a smaller component d_{z^2} on Rh. It overlaps well with 3σ on COCH₃ and is destabilised. Note that this overlap is in-phase (and thus bonding) with respect to the iron centres but out of phase with respect to the rhodium atom. $3a'$ also interacts to a lesser extent with COCH₃ 3π , and mixes with $2a'$ to give rise to MO-58.

$5a''$ is again mainly localised on the two iron atoms and comprised of an out of phase combination of (mainly) d_{xz} , with a small contribution from d_{xz} on Rh. This fragment is well hybridised to interact with COCH₃ 2π leading to a π bonding combination with respect to the two iron atoms but antibonding with respect to the Rh centre. It is strongly stabilised and MO-59 is primarily this in phase combination.

The two major interactions thus far discussed favour a closer association of the COCH₃ ligand with the iron rather than rhodium centres. $4a'$ however is mainly localised on Rh being primarily d_{yz} with some d_{yz} from the Fe atoms. In-phase interaction with COCH₃ 3π produces the HOMO MO-56, the overlap being optimised by a closer association with the rhodium atom. The observed equilibrium geometry is evidently a compromise between these opposing factors, and leads overall to a greater interaction with the two iron atoms. This is reflected in the differing overlap populations (Fe-C 0.58, Rh-C 0.37). Due to the relatively small separations between $4a'$ and $5a''$ and also between 2π and 3π , there is a tiny barrier to rotation about the CO vector of the COCH₃ ligand (ca. 5 kJ mol⁻¹) consistent with the NMR evidence of a low energy fluxional process.



From the above discussed π -type interactions there are two orientations of the COCH₃ ligand that are favoured electronically, those with the plane of COCH₃ either parallel (A), or perpendicular (B) to the Fe-Fe vector. Although geometry A

is at slightly lower energy, the difference is marginal and non-bonded repulsive interactions will also play a part in determining the final geometry.

The isolated LUMO is an in-plane metal-metal antibonding orbital with negligible alkylidyne carbon content. The next two virtual orbitals MOs 53 and 54 have significant contributions of 7.5 and 8.5% respectively, from this carbon atom, and according to Fenske's analysis [53] may be important in determining the paramagnetic contribution to its downfield ^{13}C chemical shift. It is interesting to note further that the overlap populations between the metal atoms are substantially different (Rh-Fe(1) 0.140, Rh-Fe(2) 0.142, Fe(1)-Fe(2) 0.019), leading to a conclusion of much weaker direct metal-metal bonding along the hydrido-bridged Fe-Fe vector [48,49c]. The Fe-Fe overlap population in the cluster fragment is 0.177 and the reduction in going to complex **5** is presumably mainly due to the stabilisation of $5a''$, which is antibonding with respect to the iron-iron vector.

The neutral (hypothetical) linear fragment COCH_3 has a formal C-O (Me) bond order of 2.5. The 2π and 3π levels are C-O antibonding and population of these levels by donation from cluster orbitals will reduce this multiple bond character. Since 2π and 3π are close in energy to $4a'$ and $5a''$, the COCH_3 ligand is a very effective π acid, in common with other alkylidynes [50]. The observed C-O(Me) bond length in complex **5** of 1.312(4) Å is intermediate between a single and double bond, and consistent with extensive π back donation from cluster orbitals. This then causes bending of our conceptual linear COCH_3 ligand, behaviour paralleled by isonitriles CNR (also strong π acceptors [54] and isoelectronic with COR^+) which are known to bend when extensive π back-donation occurs e.g. in $[\text{Fe}(\mu\text{-CNMe})(\text{CO})(\eta\text{-C}_5\text{H}_5)]_2$ [55], and $\text{Fe}(\text{CNBu}^+)_5$ [56].

Supplementary Material

Full listings of observed and calculated structure factors, bond lengths and angles are available on request from the author.

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