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The Crystal and Molecular Structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Re(CO)_5]$ and the Reactions of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_5]$ with RNC (R = t-Bu, 2,6-$Me_2C_6H_3$)

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Abstract

The crystal structure determination of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Re(CO)_5]$ (1) is reported (space group $P2_1/c$, $a = 27.737(5)$, $b = 6.922(5)$, $c = 14.654(4)$ Å, $\beta = 98.17(2)°$). Final R and R_w values were 0.031 and 0.026 ($w = k/\sigma^2(F)$). The non-bridged Fe–Re bond length is normal (2.888(1) Å, average value) and the Fe–Re–C(O) (equatorial CO) angles varied between 74° and 99° with an equatorial CO group bending in towards the cyclopentadienyl ligand. The Fe–Re–C(O) axial angle (167°) of one of the independent molecules of **1** differs markedly from 180°. This CO ligand is, however, almost perpendicular to the plane of the equatorial CO ligands on Re.

The synthesis and characterization of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_5]$ and its reactions with RNC (R = t-Bu, 2,6-$Me_2C_6H_3$) are also reported. In all the reactions studied the products $[(\eta^5\text{-}C_9H_7)FeRe(CO)_{7-x}(CNR)_x]$ ($x = 1$–3) were characterized and revealed substitution only on the Re atom. The attempted crystal structure determination of the unsubstituted dimer complex (twinned crystal) is also described.

Introduction

In our studies of the synthesis and structures of a series of homonuclear bimetallic transition metal carbonyl complexes we have observed that the metal–metal bond length is hardly affected by substitution of one CO by isocyanides or phosphines [1, 2]. However, a recent structure determination of $[MnRe(CO)_{10}]$ [3], a heteronuclear bimetallic complex, indicated a bond length much shorter than would have been predicted from a comparison with the bond lengths found in either $[M_2(CO)_{10}]$ (M = Mn, Re) [4, 5] or $[MnRe(CO)_9(CNR)]$ [6].

The crystal structure determination of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_5]$ (**2**) has been reported previously [7] and we recently reported the crystal structure determinations of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2M(CO)_4(CNBu\text{-}t)]$ (M = Mn (**3**), Re (**4**)) [8]. A comparison of the metal–metal bond lengths of **2** and **3** again indicated little effect of the replacement of CO by RNC. In this publication we wish to report on the results of the crystal structure determination of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Re(CO)_5]$ (**1**). This structure determination was undertaken partially to establish the Fe–Re bond length and to compare it with the Fe–Re bond length of **2**, and also to allow us to investigate further the factors which affect the Fe–Re–CO angles, which in some instances tend to differ markedly from 90°. The synthesis, reactions with RNC and our attempt to determine the crystal structure of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_5]$ (**5**) are also reported in this study.

Experimental

$[Re_2(CO)_{10}]$ was purchased from Strem Chemicals and the PdO catalyst from Johnson-Matthey chemicals. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Re(CO)_5]$ and $[(\eta^5\text{-}C_9H_7)Fe(CO)_2I]$ were synthesized by literature procedures [8–10]. All reactions were performed under nitrogen in the dark using foil wrapped flasks. Solvents were routinely dried and distilled.

IR spectra were recorded on a Perkin-Elmer 580B spectrometer and NMR spectra on a Bruker AC 200 NMR spectrometer. Melting points were recorded on a Kofler micro hot-stage apparatus and are uncorrected. Microanalyses were performed by the Microanalytical laboratories, CSIR, Pretoria. Photochemical decomposition reactions were performed using low pressure Hanovia 100 W and 450 W lamps.

$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_5]$

$[(\eta^5\text{-}C_9H_7)Fe(CO)_2I]$ (2.25 mmol) [10] was added to $Na[Re(CO)_5]$ [11] prepared from $[Re_2$-

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TABLE I. ^{1}H NMR Data for the Carbonyl Complexes Prepared in this Work

Complex	δ (ppm)^{a,b}				
	Indenyl				Me
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_5]$	7.08m	6.79m	4.58d	4.48t	
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_4(CNBu\text{-}t)]$	7.25m	6.87m	4.90t	4.81d	0.68s
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_3(CNBu\text{-}t)_2]$	7.40m	6.95m	5.35t	4.99d	0.89s
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_2(CNBu\text{-}t)_3]$	7.5m	7.0m	5.59t	5.08d	1.02, 1.00^c
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_4(CNC_6H_3Me_2\text{-}2,6)]^d$	7.21m	6.85m	4.88t	4.81d	1.94s
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2]^e$	7.3m	6.9m	5.29t	4.99d	2.14s
$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_2(CNC_6H_3Me_2\text{-}2,6)_3]$	7.4–6.6m		5.58t	5.06d	2.31^f

[a]Recorded in C_6D_6 relative to Me_4Si. [b]m = multiplet, t = triplet, d = doublet, s = singlet. [c]Ratio 2:1. [d]C_6H_3: 6.61–6.41 ppm. [e]C_6H_3: 6.69–6.53 ppm. [f]Unresolved.

$(CO)_{10}]$ (1 mmol) and Na/Hg (100 mg/5 ml) in THF (20 ml). Reaction progress was monitored by IR spectroscopy and was considered complete after stirring for 40 h in the dark. After pumping to dryness, the residue was taken up in benzene and centrifuged. The supernatant liquid was removed, concentrated and subjected to column chromatography (silica, eluent (a) hexane 150 ml, (b) hexane/benzene 60/40 *v*/*v*%). The required complex was isolated from a red band eluted from the column and characterized by melting point (87–89 °C); elemental analysis (calc.: C, 34.60; H, 1.63. Found: C, 35.06; H, 1.33%); IR spectroscopy (hexane ν(CO): 2098m; 2026w; 1996vs; 1975s; 1965w; 1931w) and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_4(CNR)]$ (R = t-Bu; 2,6-$Me_2C_6H_3$)

(a) PdO catalysed reaction

$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_5]$ (0.20 mmol) and RNC (1 equiv) were taken up in benzene (10 ml) at room temperature. PdO catalyst (7 mg) was added to the reaction mixture and reaction progress was monitored by IR spectroscopy. The reaction was considered complete after 10 min and the solution, after passage through a cellulose column to remove PdO, was pumped to dryness. An NMR spectrum (C_6D_6) of the crude reaction product indicated an essentially quantitative yield of the required product. Final purification was achieved by crystallization from toluene/hexane (−20 °C) to yield red crystalline materials. Characterization of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_4(CNBu\text{-}t)]$: melting point (95–96 °C), elemental analysis (calc.: C, 39.35; H, 2.97; N, 2.30. Found: C, 39.64; H, 2.39; N, 2.54%), IR spectroscopy (hexane: ν(NC): 2172m; ν(CO) 2059s; 1996vw, 1982vs, 1949sh; 1944s; 1907m) and NMR spectroscopy (Table I). Characterization of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_4(CNC_6H_3Me_2\text{-}2,6)]$: melting point (113–114 °C); elemental analysis (calc.: C, 43.91; H, 2.46; N, 2.13. Found: C, 44.20; H, 2.29; N, 2.20%); IR spectroscopy (hexane: ν(NC) 2145m; ν(CO) 2052m; 1998vw; 1985vs; 1952sh; 1946s; 1912w) and NMR spectroscopy (Table I).

(b) Thermal reaction

$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_5]$ (0.20 mmol) and t-BuNC (1 equiv) were taken up in benzene (10 ml) at room temperature. The reaction mixture was heated to 60 °C and monitoring by IR spectroscopy indicated that the reaction was complete after 5 min reaction time. Product identification and characterization was identical to that of (a) above.

Synthesis of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_3(CNR)_2]$, (R = t-BuNC, 2,6-$Me_2C_6H_3$)

$[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_5]$ (0.20 mmol) and RNC (2 equiv) were taken up in benzene (10 ml). PdO catalyst (6 mg) was added to the solution which was then brought to reflux. Reaction progress was monitored by IR spectroscopy and considered complete when the IR spectrum no longer changed with time. The solution was then cooled to room temperature and passed through a cellulose column to remove the PdO catalyst. An NMR spectrum (C_6D_6) of the crude reaction product indicated small amounts of the monosubstituted (~10%) and trisubstituted products (~5%). Purification of the required product (R = t-BuNC) was achieved by crystallization from acetone/hexane (−20 °C) to yield a red crystalline material. Attempted purification by crystallization of the complex with R = 2,6-$Me_2C_6H_3$NC was not successful. Characterization of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_3(CNBu\text{-}t)_2]$: melting point (113–114 °C); elemental analysis (calc.: C, 43.44; H, 3.80; N, 4.22. Found: C, 43.92; H, 3.79; N, 4.29%); IR spectroscopy (hexane: ν(NC) 2168m, 2139m ν(CO) 2022w, 1999s, 1954vs, 1936m, 1916s, 1889m) and NMR spectroscopy (Table I). Identification of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2]$: (hexane: ν(NC) 2100m, 2060m, ν(CO) 1995s, 1949vs, 1941m, 1924s, 1900m) and NMR spectroscopy (Table I).

Crystal Structure Determination of [(η^5-C_5H_5)Fe(CO)$_2$Re(CO)$_5$] (1)

Crystal data

$C_{12}H_5O_7FeRe$, $M = 503.2$, monoclinic, space group $P2_1/c$, $a = 27.737(5)$, $b = 6.922(5)$, $c = 14.654(4)$ Å, $\beta = 98.17(2)°$, $U = 2785.0$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71073$ Å), $Z = 8$, $D_c = 1.79$ g cm^{-3}. Red needles. Crystal dimensions, 0.72 × 0.13 × 0.09 mm. $F(000) = 1872$, $\lambda = 0.71073$ Å, $\mu = 93.45$ cm^{-1}.

Data collection and processing [8]

Oscillation and Weissenberg photographs were used to establish the preliminary cell constants and space group. Nonius CAD4 diffractometer, ω–2θ mode with ω scan width = 0.60 + 0.35 tan θ, ω scan speed 0.97–5.49° min^{-1}, graphite-monochromated Mo Kα radiation; 9024 reflections measured ($3.0 \leqslant \theta \leqslant 30.0°$, $\pm h$, $+k$, $+l$) 6895 unique [merging R = 0.0124], giving 4721 with $I > 4\sigma(I)$. Empirical absorption corrections [12] were applied. Linear and approximate isotropic crystal decay, *ca.* 16%, was corrected during processing.

Structure analysis and refinement

Patterson (Re and Fe atoms), and difference Fourier techniques were employed to solve the structure, using normal heavy atom procedures. Full-matrix least-squares refinement (in two blocks for final anisotropic cycles), with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with one, overall, refined U_{iso} (=0.09(1) Å^2). The weighting scheme used was $\omega = K\sigma^2(F)$. Final R and R_w values are 0.031 and 0.026. Programs and computers used and sources of scattering factors are given in ref. 8. Final fractional coordinates and isotropic temperature factors as well as bond length and bond angle data for the two independent molecules are given in Tables II and III respectively. See also 'Supplementary Material'.

Crystal Structure Determination of 5

Crystal data: space group $P2_1/c$, $a = 6.867(1)$, $b = 33.222(1)$, $c = 7.569(1)$ Å, $\beta = 107.12(1)°$. See also 'Supplementary Material'. The structure analysis and refinement was carried out using Patterson (Fe and Re atoms), and difference Fourier techniques using normal heavy atom procedures. Full matrix least-squares refinement, using unit weights, gave a final R value of 0.0924 on a twinned crystal.

TABLE II. Fractional Coordinates (×10^4, ×10^5 for Re and Fe) and Equivalent Isotropic Temperature Factors (×10^3, ×10^4 for Re and Fe) for Non-hydrogen Atoms of [(η^5-C_5H_5)Fe(CO)$_2$Re(CO)$_5$]

	x/a	y/b	z/c	U_{eq} (Å^2)
Re	16333(1)	9321(4)	8256(2)	353(1)
Fe	8213(3)	8652(14)	18613(6)	348(2)
C(1)	1178(2)	2549(11)	2528(5)	45(2)
C(2)	542(2)	2563(11)	1084(5)	42(2)
C(3)	2132(3)	2192(11)	1755(5)	50(2)
C(4)	1810(2)	−1533(11)	1471(5)	47(2)
C(5)	1436(2)	3509(11)	309(5)	47(2)
C(6)	2101(3)	505(12)	−46(5)	57(2)
C(7)	1087(2)	−282(10)	−5(5)	43(2)
O(1)	1383(2)	3672(8)	3008(4)	70(2)
O(2)	335(2)	3652(8)	583(4)	68(2)
O(3)	2427(2)	2875(9)	2265(4)	78(2)
O(4)	1921(2)	−2943(8)	1839(4)	74(2)
O(5)	1342(2)	5013(8)	25(4)	69(2)
O(6)	2353(2)	280(10)	−560(4)	82(2)
O(7)	772(2)	−923(8)	−485(4)	61(1)
C(8)	761(3)	−2201(10)	1810(5)	50(2)
C(9)	919(3)	−1585(10)	2721(5)	51(2)
C(10)	542(3)	−398(10)	2974(5)	52(2)
C(11)	167(2)	−204(10)	2224(5)	47(2)
C(12)	308(2)	−1341(10)	1492(5)	46(2)
Re′	67542(1)	7329(4)	53341(2)	397(1)
Fe′	57637(3)	8983(14)	44134(6)	383(2)
C(1′)	5692(3)	−1397(11)	4844(5)	50(2)
C(2′)	5637(3)	2061(11)	5404(5)	48(2)
C(3′)	6726(3)	−1711(11)	4634(5)	51(2)
C(4′)	6944(2)	2094(11)	4245(6)	54(2)
C(5′)	6503(3)	−620(10)	6416(6)	51(2)
C(6′)	7422(3)	470(13)	5898(5)	62(2)
C(7′)	6663(3)	3288(11)	5898(5)	54(2)
O(1′)	5619(2)	−2929(8)	5108(5)	82(2)
O(2′)	5526(2)	2831(9)	6043(4)	72(2)
O(3′)	6709(2)	−3105(8)	4211(4)	76(2)
O(4′)	7061(2)	2864(9)	3635(4)	75(2)
O(5′)	6351(2)	−1279(8)	6997(4)	77(2)
O(6′)	7818(2)	311(10)	6213(4)	90(2)
O(7′)	6618(2)	4748(8)	6249(4)	81(2)
C(8′)	5181(3)	1096(15)	3361(5)	72(3)
C(9′)	5362(3)	2920(14)	3580(6)	70(3)
C(10′)	5857(3)	2993(13)	3412(5)	60(2)
C(11′)	5964(3)	1141(15)	3082(5)	74(3)
C(12′)	5557(4)	−22(14)	3058(5)	74(3)

Results and Discussion

The X-ray crystal structure determination of **1** shows that there are no bridging CO groups and the M–M bond length (2.890(1), 2.886(1) Å) and electron counting rules [13] are consistent with the molecule being held together by a single bond. The geometry around the Re and Fe atoms is close to octahedral for both atoms (the cyclopentadienyl ring occupies three coordination sites) [14] (Fig. 1).

Bond length and bond angle data for the two independent molecules of **1** are given in Table III. However pertinent data have also been included in Table IV which also includes data for structures **2**, **3** and **4**. Newman projections of the 4 different

TABLE III. Bond Lengths (Å) and Angles (°) for Non-hydrogen Atoms of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Re(CO)_5]$

Re–Fe	2.890(1)	Re–C(3)	1.997(8)
Re–C(4)	1.978(7)	Re–C(5)	1.984(8)
Re–C(6)	1.968(8)	Re–C(7)	1.990(7)
Fe–C(1)	1.738(8)	Fe–C(2)	1.740(7)
Fe–C(8)	2.129(7)	Fe–C(9)	2.107(7)
Fe–C(10)	2.094(6)	Fe–C(11)	2.098(6)
Fe–C(12)	2.105(6)	C(1)–O(1)	1.143(8)
C(2)–O(2)	1.148(8)	C(3)–O(3)	1.131(8)
C(4)–O(4)	1.137(8)	C(5)–O(5)	1.138(8)
C(6)–O(6)	1.109(8)	C(7)–O(7)	1.132(7)
C(8)–C(9)	1.411(10)	C(8)–C(12)	1.407(9)
C(9)–C(10)	1.421(9)	C(10)–C(11)	1.407(9)
C(11)–C(12)	1.430(9)	Re′–Fe′	2.886(1)
Re′–C(3′)	1.974(8)	Re′–C(4′)	1.987(8)
Re′–C(5′)	2.047(8)	Re′–C(6′)	1.928(7)
Re′–C(7′)	1.984(8)	Fe′–C(1′)	1.732(8)
Fe′–C(2′)	1.739(8)	Fe′–C(8′)	2.073(7)
Fe′–C(9′)	2.076(8)	Fe′–C(10′)	2.106(7)
Fe′–C(11′)	2.109(7)	Fe′–C(12′)	2.088(8)
C(1′)–O(1′)	1.156(8)	C(2′)–O(2′)	1.157(8)
C(3′)–O(3′)	1.145(8)	C(4′)–O(4′)	1.128(8)
C(5′)–O(5′)	1.102(8)	C(6′)–O(6′)	1.135(8)
C(7′)–O(7′)	1.149(8)	C(8′)–C(9′)	1.379(11)
C(8′)–C(12′)	1.419(11)	C(9′)–C(10′)	1.431(10)
C(10′)–C(11′)	1.416(11)	C(11′)–C(12′)	1.383(11)
Fe–Re–C(3)	99.5(2)	Fe–Re–C(4)	83.9(2)
C(3)–Re–C(4)	87.2(3)	Fe–Re–C(5)	91.2(2)
C(3)–Re–C(5)	89.7(3)	C(4)–Re–C(5)	173.7(3)
Fe–Re–C(6)	166.7(2)	C(3)–Re–C(6)	93.0(3)
C(4)–Re–C(6)	92.3(3)	C(5)–Re–C(6)	93.4(3)
Fe–Re–C(7)	74.4(2)	C(3)–Re–C(7)	173.9(3)
C(4)–Re–C(7)	92.5(3)	C(5)–Re–C(7)	90.1(3)
C(6)–Re–C(7)	93.1(3)	Re–Fe–C(1)	82.0(2)
Re–Fe–C(2)	87.3(2)	C(1)–Fe–C(2)	94.6(3)
Re–Fe–C(8)	93.5(2)	C(1)–Fe–C(8)	136.4(3)
C(2)–Fe–C(8)	128.7(3)	Re–Fe–C(9)	106.4(2)
C(1)–Fe–C(9)	100.9(3)	C(2)–Fe–C(9)	160.5(3)
C(8)–Fe–C(9)	38.9(3)	Re–Fe–C(10)	144.9(2)
C(1)–Fe–C(10)	95.0(3)	C(2)–Fe–C(10)	127.7(3)
C(8)–Fe–C(10)	64.9(3)	C(9)–Fe–C(10)	39.6(2)
Re–Fe–C(11)	155.0(2)	C(1)–Fe–C(11)	122.6(3)
C(2)–Fe–C(11)	94.8(3)	C(8)–Fe–C(11)	65.8(3)
C(9)–Fe–C(11)	66.9(3)	C(10)–Fe–C(11)	39.2(2)
Re–Fe–C(12)	115.2(2)	C(1)–Fe–C(12)	160.3(3)
C(2)–Fe–C(12)	95.7(3)	C(8)–Fe–C(12)	38.8(2)
C(9)–Fe–C(12)	66.1(3)	C(10)–Fe–C(12)	65.5(3)
C(11)–Fe–C(12)	39.8(3)	Fe–C(1)–O(1)	174.4(6)
Fe–C(2)–O(2)	176.4(6)	Re–C(3)–O(3)	177.5(7)
Re–C(4)–O(4)	178.6(6)	Re–C(5)–O(5)	177.2(6)
Re–C(6)–O(6)	177.7(7)	Re–C(7)–O(7)	178.1(7)
Fe–C(8)–C(9)	69.7(4)	Fe–C(8)–C(12)	69.6(4)
C(9)–C(8)–C(12)	109.2(7)	Fe–C(9)–C(8)	71.4(4)
Fe–C(9)–C(10)	69.7(4)	C(8)–C(9)–C(10)	106.2(7)
Fe–C(10)–C(9)	70.7(4)	Fe–C(10)–C(11)	70.5(4)
C(9)–C(10)–C(11)	110.0(7)	Fe–C(11)–C(10)	70.2(4)
Fe–C(11)–C(12)	70.4(4)	C(10)–C(11)–C(12)	106.4(6)
Fe–C(12)–C(8)	71.5(4)	Fe–C(12)–C(11)	69.8(4)
C(8)–C(12)–C(11)	108.2(6)	Fe′–Re′–C(3′)	80.0(2)
Fe′–Re′–C(4′)	87.1(2)	C(3′)–Re′–C(4′)	89.1(3)

(continued)

TABLE III. *(continued)*

Fe'–Re'–C(5')	88.5(2)	C(3')–Re'–C(5')	91.0(3)
C(4')–Re'–C(5')	175.5(3)	Fe'–Re'–C(6')	176.1(3)
C(3')–Re'–C(6')	96.1(3)	C(4')–Re'–C(6')	92.3(3)
C(5')–Re'–C(6')	92.2(3)	Fe'–Re'–C(7')	89.4(2)
C(3')–Re'–C(7')	169.3(3)	C(4')–Re'–C(7')	88.6(3)
C(5')–Re'–C(7')	90.4(3)	C(6')–Re'–C(7')	94.5(3)
Re'–Fe'–C(1')	86.8(2)	Re'–Fe'–C(2')	85.4(2)
C(1')–Fe'–C(2')	94.2(3)	Re'–Fe'–C(8')	160.0(2)
C(1')–Fe'–C(8')	102.4(3)	C(2')–Fe'–C(8')	111.2(4)
Re'–Fe'–C(9')	134.3(3)	C(1')–Fe'–C(9')	138.9(4)
C(2')–Fe'–C(9')	91.4(3)	C(8')–Fe'–C(9')	38.8(3)
Re'–Fe'–C(10')	98.6(2)	C(1')–Fe'–C(10')	156.6(4)
C(2')–Fe'–C(10')	108.9(4)	C(8')–Fe'–C(10')	66.2(3)
C(9')–Fe'–C(10')	40.0(3)	Re'–Fe'–C(11')	94.4(2)
C(1')–Fe'–C(11')	118.0(4)	C(2')–Fe'–C(11')	147.8(4)
C(8')–Fe'–C(11')	65.6(3)	C(9')–Fe'–C(11')	65.9(3)
C(10')–Fe'–C(11')	39.3(3)	Re'–Fe'–C(12')	123.2(3)
C(1')–Fe'–C(12')	92.1(4)	C(2')–Fe'–C(12')	151.0(4)
C(8')–Fe'–C(12')	39.9(3)	C(9')–Fe'–C(12')	66.0(4)
C(10')–Fe'–C(12')	65.9(3)	C(11')–Fe'–C(12')	38.5(3)
Fe'–C(1')–O(1')	176.4(7)	Fe'–C(2')–O(2')	176.3(7)
Re'–C(3')–O(3')	178.6(7)	Re'–C(4')–O(4')	178.7(7)
Re'–C(5')–O(5')	176.6(7)	Re'–C(6')–O(6')	178.7(8)
Re'–C(7')–O(7')	177.9(8)	Fe'–C(8')–C(9')	70.7(4)
Fe'–C(8')–C(12')	70.6(5)	C(9')–C(8')–C(12')	108.3(8)
Fe'–C(9')–C(8')	70.5(5)	Fe'–C(9')–C(10')	71.1(4)
C(8')–C(9')–C(10')	108.5(8)	Fe'–C(10')–C(9')	68.9(4)
Fe'–C(10')–C(11')	70.5(5)	C(9')–C(10')–C(11')	106.2(8)
Fe'–C(11')–C(10')	70.2(4)	Fe'–C(11')–C(12')	69.9(5)
C(10')–C(11')–C(12')	109.0(8)	Fe'–C(12')–C(8')	69.5(5)
Fe'–C(12')–C(11')	71.6(5)	C(8')–C(12')–C(11')	107.9(9)

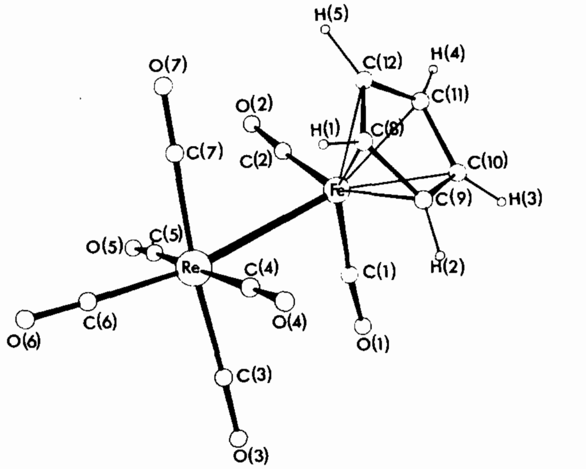


Fig. 1. ORTEP diagram of one of the two independent molecules of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Re(CO)_5]$ (1).

complexes are shown in Fig. 2 and together with the data in Table IV allow for a comparison of the four related structures to be readily made.

The numbering system used is the same as that used in ref. 8 and the data for **2** [7] have also been transposed into this numbering system.

From the Tables the following can be noted:

(i) The M–M bond length of **1**, (2.890(1), 2.886(1) Å) is similar to that of **4** (2.893 Å). Thus, isocyanide substitution has a negligible effect on the Fe–Re bond length.

(ii) The two independent molecules of **1** indicate that the cyclopentadienyl ring has shifted w.r.t. C(4)–O(4). This has a large effect on the Fe–Re–C(3) angle and a complementary effect on the Fe–Re–C(7) angle for both molecules of **1**. The CO group closest to the ring bends in towards the ring. A similar effect is observed for structures **2**–**4** (and **5**).

(iii) If the four equatorial CO groups define a plane then the axial CO (C(6)–O(6)) should be perpendicular to this plane. This is observed. Since this plane is distorted by the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ unit the Fe–Re–C(6) angle differs from 180°. Indeed the angle is equal to 167(1)° and 176(1)° for the two molecules with the displacement from 180° being in the direction of the CO which bends towards the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ unit. Similar displacements are observed for structures **2**–**4** (and **5**).

(iv) Torsion angles (Table V) reflect the movement of the ring relative to the CO groups on Re.

TABLE IV. Selected Bond Length (Å) and Bond Angle (°) Data for **1**–**4**

	1		**2**		**3**	**4**
	Molecule 1	Molecule 2	Molecule 1	Molecule 2		
Fe–M	2.890	2.886	2.839	2.843	2.841	2.893
Fe–M–C3	99.5	80.0	95.1	95.5	74.8	89.0
Fe–M–C4	83.9	87.1	83.0	80.4	89.9	86.7
Fe–M–C5	91.2	88.5	91.6	93.5	84.3	89.2
Fe–M–C6	166.7	176.1	168.5	169.1	167.8	176.9
Fe–M–C7	74.4	89.4	76.2	78.3	97.1	84.7
M–Fe–C1	82.0	86.8	83.5	86.0	81.7	85.8
M–Fe–C2	87.3	85.4	88.3	85.0	87.3	83.0
C1–Fe–C2	94.6	94.2	94.8	94.7	93.5	91.6
M–Fe–C8	93.5	160.0	94.8	95.2	118.0	97.3
M–Fe–C9	106.4	134.3	108.2	111.3	156.7	92.8
M–Fe–C10	144.9	98.6	146.0	149.7	143.7	123.1
M–Fe–C11/15	155.0	94.4	155.0	153.5	106.7	159.6
M–Fe–C12/16	155.2	123.2	116.0	114.3	94.5	132.8
Fe–C8	2.129	2.073	2.130	2.131	2.094	2.130
Fe–C9	2.107	2.076	2.134	2.101	2.080	2.137
Fe–C10	2.094	2.106	2.077	2.096	2.095	2.113
Fe–C11/15	2.098	2.109	2.073	2.078	2.104	2.116
Fe–C12/16	2.105	2.088	2.116	1.102	1.151	1.115

TABLE V. Selected Torsion Angles (°) for **1**–**4**

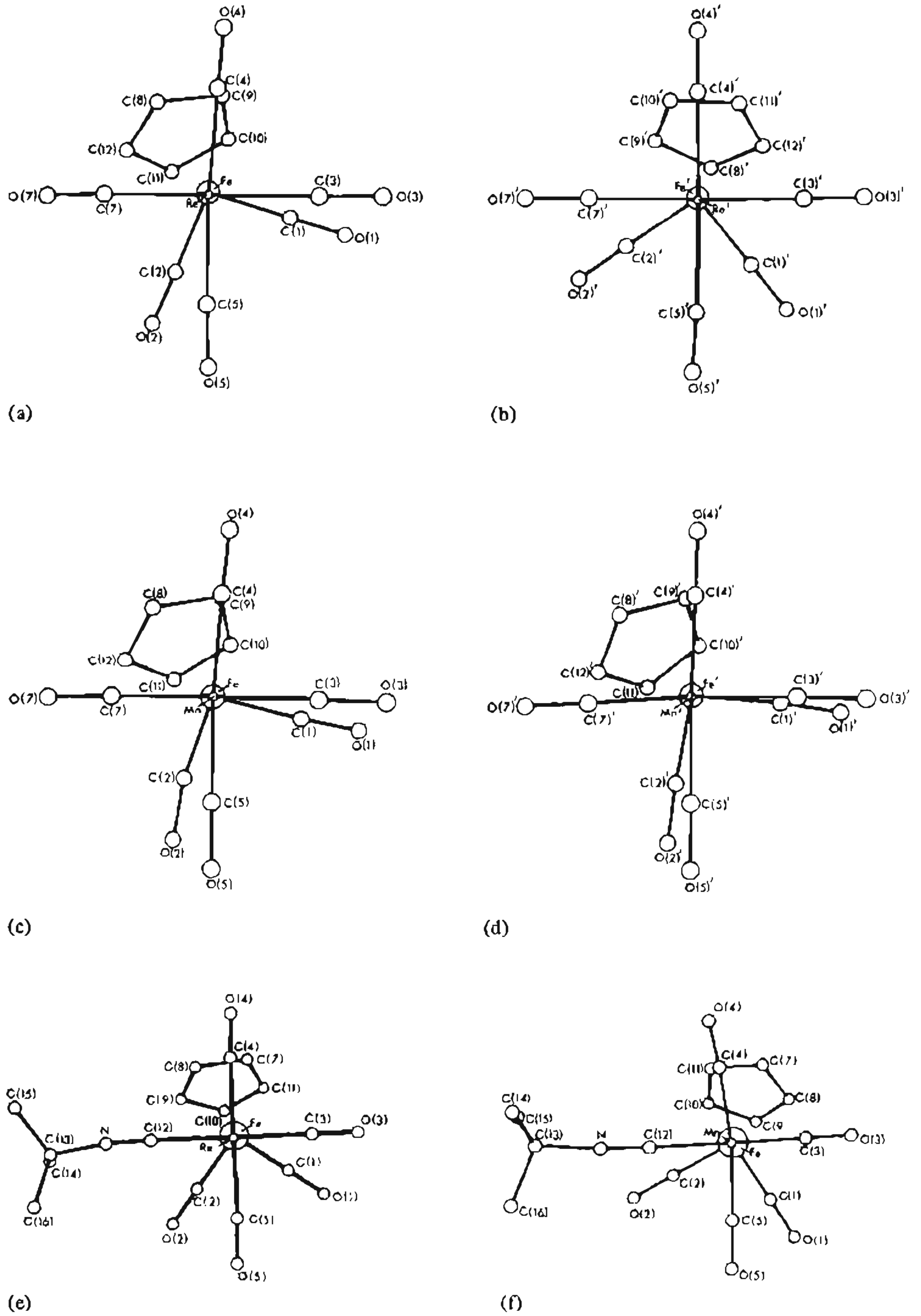
	1		**2**		**3**	**4**
	Molecule 1	Molecule 2	Molecule 1	Molecule 2		
C1–Fe–M–C3	16.47	52.47	12.41	4.96	61.2	35.0
C2–Fe–M–C5	21.49	55.22	18.51	10.15	61.9	37.2
C8–Fe–M–C4	−34.08	73.04	−38.07	−43.04		
C8–Fe–M–C7	60.20	15.56	56.03	52.55		
C9–Fe–M–C4	3.17	−65.97	0.00	−5.84		
C9–Fe–M–C3	−82.85	23.68	−87.56	−93.51		

(v) It is clear that electronic factors [15] as well as steric factors affect the Fe–Re–C(O) (CO equatorial) bond angles.

The complex $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_5]$ (**5**) was also synthesized to compare the effect of the replacement of $(\eta^5\text{-}C_5H_5)$ by $(\eta^5\text{-}C_9H_7)$ on the chemical and physical properties of the Fe–Re dimers. The new complex **5** was synthesized by conventional methodology and was characterized by spectroscopic techniques (see 'Experimental') as well as chemical reactions.

In a recent publication [8] we reported that substitution reactions of **1**, under a variety of conditions, generated the Re substituted complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Re(CO)_4L]$ (L = isocyanide, group 15 donor ligand). Since the indenyl ligand is known to increase the substitution rates of CO ligands relative to the $\eta^5\text{-}C_5H_5$ ligand [16] we had anticipated that reaction at Fe might have occurred. However reaction of **5** with 1 equivalent RNC (R = t-Bu; 2,6-$Me_2C_6H_3$) gave only $[(\eta^5\text{-}C_9H_7)Fe(CO)_2\text{-}Re(CO)_4(CNR)]$ (**6**) and small amounts of the disubstituted product $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_3\text{-}(CNR)_2]$.

Characterization of **6** as the Re substituted derivatives was readily achieved by NMR spectroscopy. The cyclopentadienyl ring in the indenyl ligand gave only two resonances in a 2:1 ratio which is characteristic of an achiral Fe centre [17]. (If substitution at Fe had occurred all the ligands attached to Fe would be different and a 1:1:1 ratio of the cyclopentadienyl resonances would have been observed.) It is also to be noted that the thermal reaction between **5** and t-BuNC was found to be much more



(a) (b) (c) (d) (e) (f)

Fig. 2. Newman projections of structures 1–4 viewed down the metal–metal bond. (a) and (b) [(η^5-C_5H_5)Fe(CO)$_2$Re(CO)$_5$] (1); (c) and (d) [(η^5-C_5H_5)Fe(CO)$_2$Mn(CO)$_5$] (2); (e) [(η^5-C_5H_5)Fe(CO)$_2$Re(CO)$_4$(CNBu-t)] (4); (f) [(η^5-C_5H_5)Fe(CO)$_2$Mn(CO)$_4$(CNBu-t)] (3).

rapid than the reaction between 1 and t-BuNC under identical reaction conditions. With the reasonable assumption that CO substitution occurs directly at Re in the presence of Pd catalysts [8] it is then apparent that a 'cooperative' indenyl effect has occurred, *i.e.* an indenyl ligand can influence chemical reactivity on an adjacent metal atom.

Substitution of a second CO group on **5** by RNC was also achieved. As expected the substitution of a second CO by RNC occurred more slowly (e.g. R = t-BuNC, 24 h, 50% reaction as detected by IR spectroscopy, room temp.; 15 min complete reaction, reflux). The new complexes $[(\eta^5\text{-}C_9H_7)Fe(CO)_2\text{-}Re(CO)_3(CNR)_2]$ (R = t-Bu, $2,6\text{-}Me_2C_6H_3$) decompose rapidly on silica gel, alumina and florisil and purification was only achieved by crystallization for R = t-Bu. Elemental analyses and NMR spectroscopy readily confirmed that the new complex contained two RNC groups. Again a 2:1 ratio of the indenyl cyclopentadienyl resonances confirmed that both RNC groups were attached to the Re atom. Small amounts of another complex, believed to be $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_2(CNR)_3)]$ were also synthesized in the above reaction. No attempts were made to isolate these new complexes which could, however, be synthesized in higher yield by using 3 equivalents of RNC (e.g. R = $2,6\text{-}Me_2C_6H_3NC$, >50% yield). The 2:1 ratio of the indenyl cyclopentadienyl resonances of these new complexes again suggests that the 3 RNC groups are all attached to the Re atom.

Photolytic irradiation of **6**, monitored by NMR spectroscopy, also confirmed that the RNC ligand was attached to the Re atom. This irradiation of **6**, R = t-BuNC, yielded $[(\eta^5\text{-}C_9H_7)Fe(CO)_2]_2$ [10] as the only indenyl containing product together with numerous t-BuNC containing products which included mainly $[Re_2(CO)_8(CNBu\text{-}t)_2]$ [18] (3 h, 28% conversion, RT). Irradiation of **6**, R = 2,6-$Me_2C_6H_3NC$, yielded $[(\eta^5\text{-}C_9H_7)Fe(CO)_2]_2$ and mainly $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$ [18] (4 h, 60% conversion, RT). Similar results were obtained for the photolysis of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2Re(CO)_3\text{-}(CNBu\text{-}t)_2]$ which yielded $[(\eta^5\text{-}C_9H_7)Fe(CO)_2]_2$ and numerous t-BuNC complexes* (12 h, 46% conversion, RT). Thermal stability of the M–M bond appears to increase with RNC substitution, in contrast to studies on phosphine substituted metal dimers in which stability decreases with phosphine substitution [19]. Presumably steric effects, which influence the site of substitution amongst other factors, are responsible for this apparent change in behaviour.

An attempt was made to determine the crystal structure of **5** to ascertain whether modification of the ring system would influence the Fe–Re bond length or conformational properties of the $Re(CO)_5$ group relative to the $Fe(CO)_2$ unit. Unfortunately the crystals of **5** were found to be twinned. The structure was however solved and the data obtained confirmed the same structural features as found for **1** (i) d(Fe–Re) = 2.881(1) Å, (ii) bending out of the C(3)–O(3) ligand while C(3)–O(3) bends in towards the indenyl group. However, the data preclude us from making any further statements about the structure of **5**. Further attempts were made to grow crystals of **5** from other solvents and at low temperature but without success.

Supplementary Material

Anisotropic temperature factors for non-hydrogen atoms, fractional coordinates for hydrogen atoms and structure factor tables are available from the authors on request.

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*Possible formation of $[Re(CO)_6(CNBu\text{-}t)_4]$ detected at δ = 1.07 ppm with resonance predicted by analogy with other t-BuNC substituted products [18].