Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 34.[1] Reactions of Sulphur and Selenium with the Di-irontungsten Complexes $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me); Crystal Structures of $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$ and $[Fe_2W(\mu_3\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)]$ *

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The compound $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ reacts with sulphur or selenium in tetrahydrofuran to afford the complexes $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}E)(CO)_7(\eta\text{-}C_5H_5)]$ (E = S or Se). Related tricapping sulphur and selenium complexes have been prepared from the species $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$. The structure of $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$ has been established by *X*-ray diffraction. The sulphur atom asymmetrically bridges the metal atom triangle [Fe–S 2.205(5) and 2.264(7), W–S 2.322(4) Å], and the two Fe–W bonds are asymmetrically bridged by a CO group [W–C–O 163(1)°] and a tolylmethylidyne ligand [μ-C–W 1.87(3), μ-C–Fe 2.12(1) Å], respectively. The methylmethylidyne di-irontungsten cluster $[Fe_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ also reacts with sulphur and with selenium affording the complexes $[Fe_2W(\mu\text{-}CMe)(\mu_3\text{-}E)(CO)_7(\eta\text{-}C_5H_5)]$ (E = S or Se) and $[Fe_2W(\mu_3\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)]$. The structure of the latter has been established by *X*-ray diffraction, leading to the characterisation of the thioacyl ligand which triply bridges the Fe_2W triangle, the C–S vector being parallel to the Fe–Fe edge so that the ligand is σ-bonded to the iron atoms *via* C–Fe and S–Fe bonds and η^2-co-ordinated to the tungsten. In hot tetrahydrofuran, the compound $[Fe_2W(\mu_3\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)]$ loses a molecule of CO and rearranges to the species $[Fe_2W(\mu\text{-}CMe)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$, the C–S bond breaking in this process. The n.m.r. data (^1H and $^{13}C\text{-}\{^1H\}$) for the new compounds are reported and discussed.

The compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) have proved to be useful precursors for the synthesis of metal cluster compounds in which alkylidyne groups bridge metal–metal bonds.[1–3] Those species in which the μ-CR groups triply bridge a triangle of metal atoms are of particular interest, since they allow the reactivity of the organic ligand to be explored when activated by three metal centres. Reaction pathways for alkylidyne groups in metal clusters may be relevant to the behaviour of these fragments when bonded to metal surfaces where they are thought to play a pivotal role in heterogeneous reactions.[4–6] Now that several heteronuclear trimetal clusters containing μ_3-CR ligands[2] are available it is possible to investigate the chemistry of these alkylidyne groups in detail. Herein we describe reactions of the di-irontungsten compounds $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) (**1**) with sulphur and with selenium. Sulphur, either in elemental form, or as H_2S or mercaptan (R′SH), is a frequent contaminant of feed-stocks in heterogeneous reactions catalysed by metals. It was, therefore, of interest to establish the nature of any reaction which occurred between sulphur and a trimetal complex containing a μ_3-CR ligand.

Results and Discussion

Compound (**1a**; R = C_6H_4Me-4), employed in this study, has been reported earlier.[7] The methylmethylidyne analogue (**1b**), which was also required, had not been prepared previously. It was obtained by treating $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ with excess of $[Fe_2(CO)_9]$ in diethyl ether, and was characterised by microanalysis and by its spectroscopic properties (Tables 1 and 2). The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum, when measured at room temperature, showed only one broad resonance for the CO ligands (Table 2). However, when the spectrum was measured at −50 °C, three signals [δ 256.8 (μ-CO), 212.8 (FeCO), and 209.6 p.p.m. (WCO)] were observed. Hence although site exchange of CO ligands between different metal centres has ceased at −50 °C, exchange within the $Fe(CO)_3$ groups is still occurring.

The synthesis of (**1b**), even when using excess of $[Fe_2(CO)_9]$, is accompanied by formation of trace quantities of the cluster compound $[FeW_2(\mu_3\text{-}MeC_2Me)(CO)_6(\eta\text{-}C_5H_5)_2]$. In the syntheses of (**1a**), a similar alkyne-bridged compound $[FeW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ is also formed. If excess of the alkylidyne reagents $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) are employed in these reactions the ironditungsten compounds are the major products.

Complex (**1a**) reacts with elemental sulphur in tetrahydrofuran (thf) at room temperature to give a dark red crystalline complex (**2**) in essentially quantitative yield. Data for the compound are given in Tables 1 and 2. The same species is formed in good yield when (**1a**) is treated with either H_2S or Bu^tSH. The compound $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6(\eta\text{-}C_5H_5)]$ (**3**), a derivative of (**1a**) containing a bis(diphenylphosphino)methane (dppm) ligand spanning the

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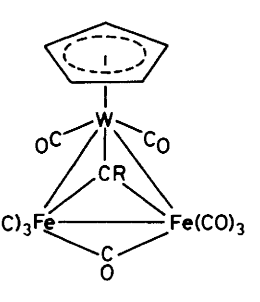
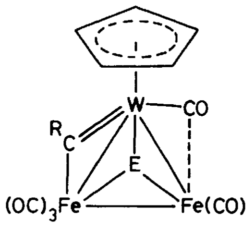
* 1,1,1,2,2,2,3-Heptacarbonyl-3-η-cyclopentadienyl-μ_3-thio-1,3-μ-*p*-tolylmethylidyne-*triangulo*-di-irontungsten and 1,1,1,2,2,2,3,3-octacarbonyl-3-η-cyclopentadienyl-μ_3-[η^2-thioacetyl-*S*(Fe^1, W), *C*(Fe^2, W)]-*triangulo*-di-irontungsten.

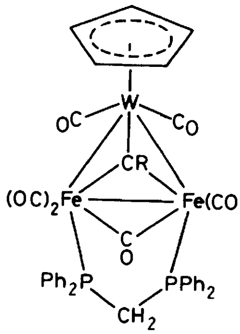
Supplementary data available (No. SUP 56198, 13 pp.): thermal parameters, complete bond parameters, H-atom co-ordinates for (**7**). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



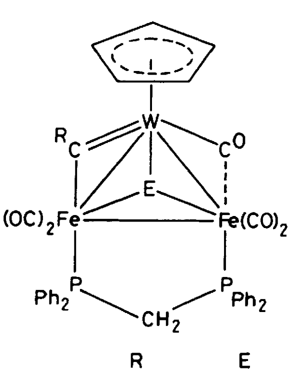
R
(1a) C_6H_4Me-4
(1b) Me



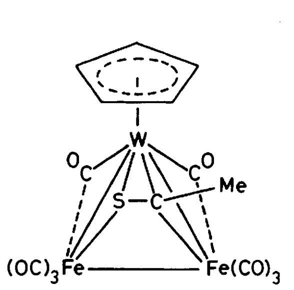
	R	E
(2)	C_6H_4Me-4	S
(5)	C_6H_4Me-4	Se
(8)	Me	S
(9)	Me	Se



R
(3) C_6H_4Me-4



	R	E
(4)	C_6H_4Me-4	S
(6)	C_6H_4Me-4	Se



(7)

iron–iron bond,[7] also reacts with sulphur, but it is necessary to reflux the reactants in thf solution for the product (4) to be formed at an appreciable rate. The ^{13}C-$\{^1H\}$ spectra (Table 2) revealed resonances [δ 313.7 for (2) and 313.9 p.p.m. for (4)] characteristic of bridging μ-*C*R groups. However, these chemical shifts are in the range observed for structures in which the ligated carbon atoms of the tolylmethylidyne group are bridging two rather than three metal atoms.[8] In the ^{13}C-$\{^1H\}$ n.m.r. spectra of (1a) and (3) the μ_3-C nuclei are less deshielded, resonating at 282.6 and 272.1 p.p.m., respectively.[7] Selenium also reacts with compounds (1a) and (3), but it is necessary to heat the reactants in thf. Data for the two products (5) and (6) are given in Tables 1 and 2; the ^{13}C-$\{^1H\}$ n.m.r. spectra are again revealing, showing resonances [δ 318.5 for (5) and 319.5 p.p.m. for (6)] characteristic for μ-*C*R groups bridging two metal centres. Evidently compounds (2), (4), (5), and (6) have similar structures. Fortunately suitable crystals of (2) were available for an *X*-ray diffraction study.

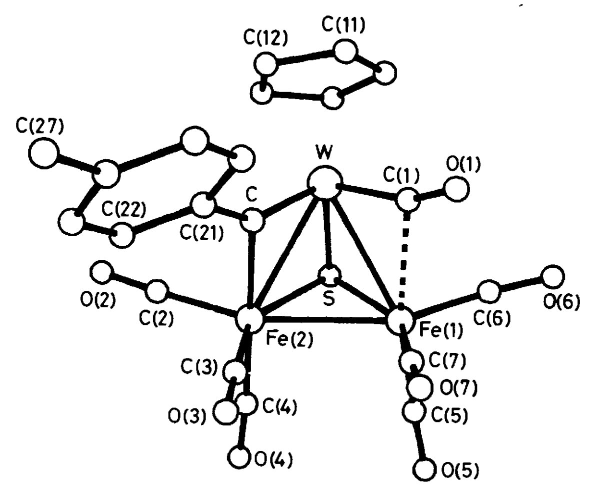


Figure 1. The molecular structure of $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$ (2) showing the atom numbering scheme

The results are summarised in Table 3, and the molecule is shown in Figure 1 with the atom labelling scheme. It will be seen that a sulphur atom asymmetrically caps a triangle formed by the metal atoms. One of the Fe–W edges of the cluster is bridged by a CC_6H_4Me-4 group and the other is semi-bridged by a carbonyl ligand. Each iron atom carries three terminally bound CO groups, and the tungsten atom is ligated by the C_5H_5 moiety.

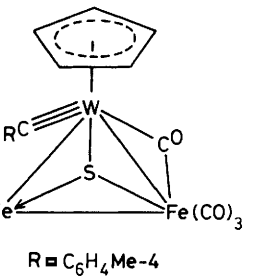
The iron–sulphur bonds [Fe(1)–S 2.205(5) and Fe(2)–S 2.264(7) Å] are somewhat longer than those reported for the complexes $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ [2.158(4) Å][9] and $[Fe_3(\mu_3\text{-}CO)(\mu_3\text{-}S)(CO)_9]$ [2.21(1) Å],[10] probably due to the incorporation of the large tungsten atom into the μ_3-SFe_2W core of (2). The W–S separation is 2.322(4) Å, and is thus very similar to those found in the clusters $[CoFeW(\mu_3\text{-}S)(CO)_7(PMePr^nPh)(\eta\text{-}C_5H_5)]$ [2.348(3) Å] and $[Co_2W(\mu_3\text{-}S)\{\mu\text{-}Me_2AsCo(CO)_3AsMe_2\}(CO)_6(\eta\text{-}C_5H_5)]$ [2.357(3) Å].[11]

The iron–iron distance [2.645(3) Å] may be compared with those in (1a) [2.538(2) Å][7] and in $[Fe_3(\mu_3\text{-}CO)(\mu_3\text{-}S)(CO)_9]$ [2.61(1) Å].[10] The iron–tungsten separations [Fe(1)–W 2.777(2), Fe(2)–W 2.742(3) Å] are slightly shorter than those in (1a) [mean 2.781(2) Å], as expected, since the iron–tungsten bonds in (2) are bridged by μ-CC_6H_4Me-4 and CO ligands. The latter group is clearly semi-bridging [W–C(1) 1.98(2), Fe(1) ··· C(1) 2.51(2) Å; W–C(1)–O(1) 162.8(13)°]. The tolylmethylidyne group is also best regarded as semi-bridging, with only a weak interaction with Fe(2). Thus the μ-C–W separation [1.87(3) Å] is substantially shorter than that found [2.14(2) Å] for the C=W bond in $[W(=CPh_2)(CO)_5]$,[12] and appreciably shorter than the μ-C–W distances in several dimetal complexes containing unsaturated ring systems $M(\mu\text{-}CC_6H_4Me\text{-}4)W$ (M = Co, Rh, Ti, Pt, or Cr: 1.91(2)—2.025(6) Å].[8] In the recently reported[13] trimetal compound $[ReW_2(\mu\text{-}Br)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)_2]$, which contains a tolylmethylidyne ligand edge-bridging a W–W bond, the μ-C–W separation [mean 1.97(1) Å] is also appreciably longer than that in (2). Indeed, in the latter the μ-C–W bond is close to that found [1.82(2) Å] in the monotungsten compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.[14] The tight alkylidyne–tungsten bonding results in a not unexpectedly weak μ-C–Fe(2) interaction [2.12(1) Å]. The latter may be compared with the shorter μ-C–Fe distances of 1.969(5) and 2.029(6) Å in the compounds (1a)[7] and $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$,[15] respectively. These data are perhaps indicative of the

Table 1. Analytical[a] and physical data for the di-irontungsten complexes

Compound	M.p.[b] (θ_c/°C)	Colour	Yield (%)	ν(CO)/cm^{-1}	Analysis (%) C	H
(**1b**) $[Fe_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$	159—162	Brown	60	[c]2 064m, 2 023s, 2 009s, 1 999m, 1 987m, 1 981m, 1 783w	[d]29.1 (29.0)	1.2 (1.3)
(**2**) $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$	181—183	Red	95	[e]2 056s, 2 013vs, 1 992m, 1 975m, 1 953m, 1 870wbr	[f]34.6 (34.7)	1.7 (1.8)
(**4**) $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}dppm)(\mu_3\text{-}S)(CO)_5(\eta\text{-}C_5H_5)]$	180—182	Red	65	[g]1 980m, 1 943s, 1 914m, 1 890m, 1 798w	[h]46.9 (47.8)	3.3 (3.3)
(**5**) $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}Se)(CO)_7(\eta\text{-}C_5H_5)]$	196—200	Red	70	[e]2 053s, 2 011vs, 1 989m, 1 973m, 1 951m, 1 862w	32.0 (32.5)	1.6 (1.6)
(**6**) $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}dppm)(\mu_3\text{-}Se)(CO)_5\text{-}(\eta\text{-}C_5H_5)]$	204—208	Brown	50	[e]1 981m, 1 942s, 1 914m, 1 893m, 1 800w	[h]44.6 (45.8)	3.2 (3.1)
(**7**) $[Fe_2W(\mu_3\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)]$		Purple	[i]30	[c]2 061s, 2 016vs, 1 995s, 1 979m, 1 968m, 1 952w, 1 901wbr, 1 851w	27.5 (28.0)	1.2 (1.2)
(**8**) $[Fe_2W(\mu\text{-}CMe)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$	150—152	Purple	[i]30	[g]2 058m, 2 014s, 1 992m, 1 975m, 1 950m, 1 867mbr	27.4 (27.3)	1.3 (1.3)
(**9**) $[Fe_2W(\mu\text{-}CMe)(\mu_3\text{-}Se)(CO)_7(\eta\text{-}C_5H_5)]$	140—144	Red	50	[e]2 053m, 2 009s, 1 986m, 1 971m, 1 950m, 1 873w	26.0 (25.4)	2.0 (1.2)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] In cyclohexane. [d] Crystallised with half a molecule of CH_2Cl_2. [e] In thf. [f] S, 4.2 (4.6%). [g] In CH_2Cl_2. [h] Crystallised with a molecule of CH_2Cl_2. [i] Relative yields of (**7**) and (**8**) variable, see text.



importance of the canonical form for (**2**), shown above, which confers an 18-electron count at each metal centre.

The most interesting feature of the *X*-ray study on (**2**) was confirmation of the presence of an edge- rather than a triply-bridging CC_6H_4Me-4 ligand; strong evidence for which had been provided by the ^{13}C-$\{^1H\}$ n.m.r. data, discussed above. The structures of (**4**)—(**6**) are evidently similar to that of (**2**), and thus in the formation of this group of compounds, sulphur and selenium promote the transfer of the tolylmethylidyne ligand from a μ_3-CFe_2W to a μ-CFe_2W bonding mode. In an attempt to gain more information about the pathway followed in this interesting transformation, reactions between (**1b**) and sulphur and selenium were investigated to ascertain whether similar products would be obtained. There is a growing body of evidence that trimetal clusters with μ_3-alkylidyne ligands differ in reactivity depending on whether a C_6H_4Me-4 or Me substituent is bonded to the ligated carbon atom.[1]

Compound (**1b**) reacts with sulphur in thf at room temperature to produce a purple crystalline compound (**7**). Formation of the latter is often accompanied by production of a second purple complex $[Fe_2W(\mu\text{-}CMe)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$ (**8**). The two species are readily separated by column chromatography. Complex (**8**) was characterised (Tables 1 and 2) as the methylmethylidyne analogue of (**2**). The ^{13}C-$\{^1H\}$ n.m.r. spectrum showed a characteristic resonance (322.4 p.p.m.) for a methylidyne carbon nucleus spanning two metal centres, this signal being more deshielded than that found (Table 2) for this nucleus in the precursor (**1b**). The i.r. spectrum of (**8**) in the CO stretching region was very similar to that of (**2**). Selenium also reacts with (**1b**), producing a single product $[Fe_2W(\mu\text{-}CMe)(\mu_3\text{-}Se)(CO)_7(\eta\text{-}C_5H_5)]$ (**9**), data for which (Tables 1 and 2) show that it is an analogue of (**5**). The synthesis of (**9**) requires the reactants to be heated to at least 45 °C in thf, and, as

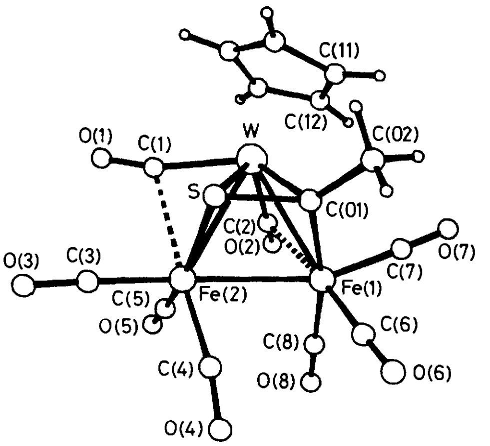


Figure 2. The molecular structure of $[Fe_2W(\mu_3\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)]$ (**7**) showing the atom numbering scheme

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the di-irontungsten complexes

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(**1b**)	[d] 4.54 (s, 3 H, Me), 5.30 (s, 5 H, C_5H_5)	285.9 (μ_3-C), 215.9 (br, CO), 90.2 (C_5H_5), 47.3 (Me)
(**2**)	[d] 2.27 (s, 3 H, Me-4), 5.70 (s, 5 H, C_5H_5), 7.10 (m, 4 H, C_6H_4)	[e] 313.7 [μ-C, *J*(WC) 159], 241.8 [WCO, *J*(WC) 191], 214.9, 214.4, 212.8, 209.8, 208.3, 202.3 (FeCO), 153.5 [C^1 (C_6H_4), *J*(WC) 27], 139.9 [C^4 (C_6H_4)], 129.9 [C^2 and C^6 (C_6H_4)], 129.0 [C^3 and C^5 (C_6H_4)], 95.3 (C_5H_5), 22.0 (Me-4)
(**4**)	2.22 (s, 3 H, Me-4), 2.70 [d of d of d, 1 H, CH_2, *J*(HH) 14, *J*(PH) 11 and 11], 4.31 [d of d of d, 1 H, CH_2, *J*(HH) 14, *J*(PH) 11 and 11], 5.75 (s, 5 H, C_5H_5), 7.13—7.41 (m, 24 H, Ph and C_6H_4)	313.9 [d, μ-C, *J*(PC) 9], 259.9 (WCO), 223.4 [d, FeCO, *J*(PC) 25], 222.7 [d, FeCO, *J*(PC) 12], 213.4 [d, FeCO, *J*(PC) 15], 209.1 [d, FeCO, *J*(PC) 19], 156.1 [C^1 (C_6H_4)], 137.0 [C^4 (C_6H_4)], 134—126 (C_6H_4 and Ph), 94.9 (C_5H_5), 44.4 [d of d, CH_2, *J*(PC) 20 and 20], 21.7 (Me-4)
(**5**)	2.28 (s, 3 H, Me-4), 5.70 (s, 5 H, C_5H_5), 7.18 (m, 4 H, C_6H_4)	318.5 [μ-C, *J*(WC) 156], 244.2 [WCO, *J*(WC) 184], 212.4, 209.2 (FeCO), 155.5 [C^1 (C_6H_4)], 139.2 [C^4 (C_6H_4)], 129.7 [C^2 and C^6 (C_6H_4)], 126.4 [C^3 and C^5 (C_6H_4)], 94.3 (C_5H_5), 21.8 (Me-4)
(**6**)	2.23 (s, 3 H, Me-4), 2.60 [d of d of d, 1 H, CH_2, *J*(HH) 13, *J*(PH) 11 and 11], 5.14 [d of d of d, 1 H, CH_2, *J*(HH) 13, *J*(PH) 11 and 11], 5.66 (s, 5 H, C_5H_5), 7.14—7.38 (m, 24 H, Ph and C_6H_4)	319.5 [d, μ-C, *J*(PC) 9], 262.9 (WCO), 222.4, 222.2, 214.6, 210.5 (FeCO), 157.4 [C^1 (C_6H_4)], 133.1 [C^4 (C_6H_4)], 134—126 (C_6H_4 and Ph), 94.0 (C_5H_5), 45.8 [d of d, CH_2, *J*(PC) 20 and 20], 21.7 (Me-4)
(**7**)	2.93 (s, 3 H, Me), 5.59 (s, 5 H, C_5H_5)	231.4 [WCO, *J*(WC) 170], 220.4 [WCO, *J*(WC) 159], 215.6, 214.3, 212.3, 211.1, 206.8 (FeCO), 174.3 [μ_3-SCMe, *J*(WC) 43], 92.7 (C_5H_5), 43.5 (Me)
(**8**)	2.35 (s, 3 H, Me), 5.75 (s, 5 H, C_5H_5)	322.4 (μ-*C*Me), 242.4 (WCO), 212.3, 209.5 (FeCO), 94.9 (C_5H_5), 48.3 (Me)
(**9**)	2.44 (s, 3 H, Me), 5.76 (s, 5 H, C_5H_5)	325.7 [μ-*C*Me, *J*(WC) 162], 243.1 [WCO, *J*(WC) 186], 211.6, 208.3 (FeCO), 92.7 (C_5H_5), 47.7 (Me)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in CD_2Cl_2, unless otherwise stated. [c] Measured in CD_2Cl_2–CH_2Cl_2, unless otherwise stated. Hydrogen-1 decoupled, δ in p.p.m. to high frequency of $SiMe_4$. [d] In $CDCl_3$. [e] Measured at −30 °C.

Table 3. Selected internuclear distances (Å) and angles (°) for $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$ (**2**)

W–Fe(1)	2.777(2)	W–Fe(2)	2.742(3)	W–S	2.322(4)	W–C	1.87(3)
W–C(1)	1.98(2)	Fe(1)–Fe(2)	2.645(3)	Fe(1)–S	2.205(5)	Fe(1) ··· C(1)	2.51(2)
Fe(1)–C(5)	1.83(2)	Fe(1)–C(6)	1.77(2)	Fe(1)–C(7)	1.77(3)	Fe(2)–S	2.264(7)
Fe(2)–C	2.12(1)	Fe(2)–C(2)	1.79(1)	Fe(2)–C(3)	1.74(3)	Fe(2)–C(4)	1.81(2)
C–C(21)	1.49(3)	C(1)–O(1)	1.17(2)	C(2)–O(2)	1.14(2)	C(3)–O(3)	1.18(3)
C(4)–O(4)	1.14(2)	C(5)–O(5)	1.13(2)	C(6)–O(6)	1.17(3)	C(7)–O(7)	1.16(3)
Fe(1)–W–Fe(2)	57.3(1)	Fe(1)–W–S	50.3(1)	Fe(2)–W–S	52.3(2)	Fe(1)–W–C	89.4(4)
Fe(2)–W–C	50.4(4)	S–W–C	102.7(5)	W–Fe(1)–Fe(2)	60.7(1)	W–Fe(1)–S	54.1(1)
Fe(2)–Fe(1)–S	54.7(2)	W–Fe(2)–Fe(1)	62.0(1)	W–Fe(2)–S	54.3(1)	Fe(1)–Fe(2)–S	52.7(1)
W–Fe(2)–C	42.9(7)	Fe(1)–Fe(2)–C	88.1(4)	S–Fe(2)–C	97.1(7)	W–S–Fe(1)	75.6(2)
W–S–Fe(2)	73.4(2)	Fe(1)–S–Fe(2)	72.6(2)	W–C–Fe(2)	86.7(8)	W–C–C(21)	146.6(12)
Fe(2)–C–C(21)	126.7(14)	W–C(1)–O(1)	162.8(13)	Fe(1)–C(1)–O(1)	122(2)	Fe(2)–C(2)–O(2)	179.8(23)
Fe(2)–C(3)–O(3)	178.2(15)	Fe(2)–C(4)–O(4)	175.7(23)	Fe(1)–C(5)–O(5)	174.8(15)	Fe(1)–C(6)–O(6)	176.9(24)
Fe(1)–C(7)–O(7)	178.5(11)						

Table 4. Selected internuclear distances (Å) and angles (°) for $[Fe_2W(\mu_3\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)]$ (**7**)

W–Fe(1)	2.757(1)	W–Fe(2)	2.765(1)	W–S	2.439(2)	W–C(01)	2.195(8)
W–C(1)	1.999(1)	W–C(2)	1.981(8)	Fe(1)–Fe(2)	2.673(2)	Fe(1)–C(01)	1.951(8)
Fe(1) ··· C(2)	2.473(8)	Fe(1)–C(6)	1.790(9)	Fe(1)–C(7)	1.788(10)	Fe(1)–C(8)	1.821(9)
Fe(2)–S	2.233(2)	Fe(2)–C(3)	1.791(8)	Fe(2)–C(4)	1.801(9)	Fe(2)–C(5)	1.789(10)
S–C(01)	1.755(8)	C(01)–C(02)	1.506(14)	C(1)–O(1)	1.173(11)	C(2)–O(2)	1.166(9)
C(3)–O(3)	1.147(11)	C(4)–O(4)	1.141(11)	C(5)–O(5)	1.139(12)	C(6)–O(6)	1.145(11)
C(7)–O(7)	1.148(12)	C(8)–O(8)	1.132(11)				
Fe(1)–W–Fe(2)	57.9(1)	Fe(1)–W–S	71.8(1)	Fe(2)–W–S	50.3(1)	Fe(1)–W–C(01)	44.6(2)
Fe(2)–W–C(01)	71.7(2)	S–W–C(01)	44.1(2)	W–Fe(1)–Fe(2)	61.2(1)	W–Fe(1)–C(01)	52.2(2)
Fe(2)–Fe(1)–C(01)	77.2(2)	W–Fe(2)–Fe(1)	60.9(1)	W–Fe(2)–S	57.3(1)	Fe(1)–Fe(2)–S	76.5(1)
W–S–Fe(2)	72.4(1)	W–S–C(01)	60.5(2)	Fe(2)–S–C(01)	94.2(3)	W–C(01)–Fe(1)	83.1(3)
W–C(01)–S	75.3(3)	Fe(1)–C(01)–S	111.1(4)	W–C(01)–C(02)	128.3(6)	Fe(1)–C(01)–C(02)	127.7(6)
S–C(01)–C(02)	116.6(6)	W–C(1)–O(1)	164.1(7)	W–C(2)–O(2)	163.1(7)	Fe(1)–C(2)–O(2)	120.6(6)
Fe(2)–C(3)–O(3)	177.6(8)	Fe(2)–C(4)–O(4)	171.5(8)	Fe(2)–C(5)–O(5)	176.6(9)	Fe(1)–C(6)–O(6)	176.3(9)
Fe(1)–C(7)–O(7)	178.3(9)	Fe(1)–C(8)–O(8)	178.1(8)				

discussed further below, this may well be the reason why a selenium analogue of (**7**) was not observed.

Compound (**7**) (Tables 1 and 2) did not contain a bridging methylmethylidyne ligand since the ^{13}C-{^{1}H} n.m.r. spectrum showed no resonance in the range δ *ca.* 230—450 p.p.m. However, a signal was observed at δ 174.3 p.p.m. with tungsten satellites [*J*(^{183}W–^{13}C) 43 Hz], and a further signal at δ 43.5 could be assigned to a methyl group since in a fully proton-coupled spectrum it appeared as a quartet [*J*(HC) 128 Hz]. Evidently (**7**) contained a CMe group bonded in some manner

Table 5. Atomic positional parameters (fractional co-ordinates; × 10^4), with estimated standard deviations in parentheses, for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2 266(1)	1 185(1)	2 062(1)	O(6)	−2 333(21)	940(6)	−2 500(16)
Fe(1)	−1 257(3)	1 554(1)	−35(2)	C(7)	−2 622(24)	1 251(7)	283(16)
Fe(2)	838(3)	2 080(1)	2 404(2)	O(7)	−3 552(19)	1 054(6)	461(15)
S	1 236(6)	2 012(2)	812(4)	C(11)	4 039(19)	397(5)	2 759(15)
C	1 982(22)	1 304(6)	3 388(16)	C(12)	5 070	791	3 865
C(1)	243(22)	650(7)	1 155(15)	C(13)	5 436	1 248	3 364
O(1)	−594(16)	240(5)	844(12)	C(14)	4 631	1 136	1 949
C(2)	2 863(22)	2 411(6)	3 891(16)	C(15)	3 768	611	1 576
O(2)	4 154(18)	2 620(6)	4 836(13)	C(21)	2 254(14)	1 079(4)	4 623(8)
C(3)	−553(20)	1 949(6)	2 796(16)	C(22)	2 641	1 416	5 696
O(3)	−1 476(19)	1 871(5)	3 086(13)	C(23)	2 764	1 185	6 779
C(4)	−264(24)	2 741(7)	1 615(17)	C(24)	2 500	617	6 789
O(4)	−949(19)	3 161(5)	1 192(15)	C(25)	2 114	280	5 715
C(5)	−2 892(23)	2 111(7)	−1 087(18)	C(26)	1 991	511	4 633
O(5)	−4 003(17)	2 425(6)	−1 787(15)	C(27)	2 559(26)	349(9)	7 945(20)
C(6)	−1 862(26)	1 187(7)	−1 513(19)				

Table 6. Atomic positional parameters (fractional co-ordinates), with estimated standard deviations in parentheses, for compound (**7**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.768 07(3)	0.842 97(2)	−0.045 00(2)	C(5)	0.526 7(11)	0.808 7(7)	0.137 4(7)
Fe(1)	0.737 69(12)	0.665 71(7)	0.010 44(8)	O(5)	0.396 6(9)	0.819 6(6)	0.139 3(6)
Fe(2)	0.733 31(13)	0.797 56(8)	0.138 43(7)	C(6)	0.862 9(11)	0.579 3(7)	0.068 8(7)
S	0.9675(3)	0.813 74(14)	0.092 9(2)	O(6)	0.949 9(9)	0.526 6(5)	0.105 1(6)
C(01)	0.930 9(9)	0.732 0(6)	0.002 8(6)	C(7)	0.720 2(11)	0.616 5(7)	−0.105 3(7)
C(02)	1.070 2(11)	0.700 2(8)	−0.039 8(9)	O(7)	0.709 2(11)	0.587 0(6)	−0.180 5(6)
C(1)	0.702 5(10)	0.939 5(7)	0.038 8(6)	C(8)	0.551 6(10)	0.621 2(6)	0.035 1(7)
O(1)	0.663 0(9)	1.008 3(5)	0.068 8(5)	O(8)	0.437 8(8)	0.591 3(5)	0.051 0(6)
C(2)	0.556 9(10)	0.787 6(6)	−0.056 7(6)	C(11)	0.869 1(14)	0.832 6(8)	−0.186 9(8)
O(2)	0.423 0(7)	0.773 4(5)	−0.078 0(5)	C(12)	0.707 8(15)	0.843 5(8)	−0.208 4(7)
C(3)	0.783 4(11)	0.873 9(6)	0.236 1(6)	C(13)	0.665 5(13)	0.927 3(8)	−0.175 8(7)
O(3)	0.816 3(10)	0.920 1(6)	0.300 7(5)	C(14)	0.802 7(15)	0.970 0(8)	−0.136 7(7)
C(4)	0.751 7(10)	0.692 7(7)	0.203 9(6)	C(15)	0.928 3(13)	0.911 7(9)	−0.140 6(8)
O(4)	0.756 0(9)	0.632 0(5)	0.253 8(5)				

to tungsten. To establish the structure of the compound an *X*-ray diffraction study was carried out.

The molecule is shown in Figure 2, and selected bond distances and angles are given in Table 4. An Fe_2W triangle forms the core of the molecule. Each iron atom carries three carbonyl ligands whilst the tungsten atom is ligated by a cyclopentadienyl group and two carbonyl ligands. The latter semi-bridge the iron–tungsten bonds [W–C(1)–O(1) 164.1(7), W–C(2)–O(2) 163.1(7)°], and are thus responsible for the resonances in the $^{13}C-\{^1H\}$ n.m.r. spectrum at δ 231.4 and 220.4 p.p.m. which show ^{183}W satellite peaks [*J*(WC) 170 and 159 Hz, respectively].

Interest centres on a thioacyl group (SCMe) which triply bridges the face of the metal atom triangle. The sulphur atom is bonded to the tungsten and to Fe(2) [W–S 2.439(2), Fe(2)–S 2.233(2) Å] and C(01) is attached to tungsten and to Fe(1) [W–C(01) 2.195(8), Fe(1)–C(01) 1.951(8) Å]. Evidently the C(01) atom is responsible for the resonance observed at δ 174.3 p.p.m. in the $^{13}C-\{^1H\}$ spectrum of (**7**), mentioned above. The thioacyl ligand is formed by combination of sulphur with the methylmethylidyne group in (**1b**). The C(01)–S vector lies parallel to the iron–iron bond, and using the notation[16] accepted for alkyne bonding in trimetal complexes the thioacyl group is $\mu_3(\eta\text{-}\|)$ bound to the metal triangle. Recently a tri-iron complex anion $[Fe_3(\mu_3\text{-}OCMe)(CO)_9]^-$ has been reported[17] in which an acyl ligand bonds to the metal triangle in a similar manner to that of the SCMe group in (**7**).

Compound (**7**) appears to be the first example of a cluster containing a thioacyl ligand bridging in the manner established by the *X*-ray diffraction study. In examining its properties the very important observation was made that on heating (**7**) in thf to *ca.* 50 °C it is converted into compound (**8**) with loss of CO. This transformation is complete in *ca.* 5 h under these relatively mild conditions. It is thus very probable that in the reactions of sulphur or selenium with the compounds (**1**) and (**3**), the various products (**2**)—(**6**), (**8**) and (**9**) are produced *via* species like (**7**) with ECR (E = S or Se, R = C_6H_4Me-4 or Me) groups. These intermediates could subsequently undergo carbon–sulphur or –selenium bond rupture, the alkylidyne group passing into an edge-bridging environment with the S or Se atoms capping the Fe_2W triangles.

Experimental

Experiments were carried out using Schlenk tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents were rigorously dried before use. Light petroleum refers to that fraction b.p. 40—60 °C. The n.m.r. measurements were made with JNM-FX 90Q and FX 200 instruments. I.r. spectra were recorded with a Nicolet 10-MX FT spectrophotometer. Compounds (**1a**) and (**3**) were prepared as described previously.[7] Analytical and spectroscopic data for the new compounds are given in Tables 1 and 2.

Synthesis of $[Fe_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**1b**).—A mixture of $[Fe_2(CO)_9]$ (1.26 g, 3.45 mmol) and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.38 g, 1.15 mmol) was stirred in diethyl ether (25 cm^3) for 24 h. Solvent was removed *in vacuo*, and the dark brown residue was dissolved in dichloromethane–light petroleum (3:2), and chromatographed on a Florisil column

(3 × 20 cm) cooled to −10 °C. Elution with the same solvent mixture afforded a brown eluate, from which solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (*ca.* 1 cm^3), and light petroleum (*ca.* 10 cm^3) added to give dark brown *crystals* of (**1b**) (0.43 g). Further elution of the chromatography column with dichloromethane–light petroleum (4:1) afforded a purple eluate which gave after removal of solvent the cluster compound [FeW$_2$(μ_3-MeC$_2$Me)(CO)$_6$(η-C$_5$H$_5$)$_2$] [Found: C, 30.7; H, 2.3. C$_{20}$H$_{16}$FeO$_6$W$_2$ requires C, 30.9; H, 2.1%]. I.r.: $\nu_{max.}$(CO) at 2 028s, 2 022s, 1 982s, 1 970s, 1 963s, 1 957s, 1 939s, 1 920s, 1 886m, and 1 828mbr cm^{-1} (in cyclohexane) (mixture of rotational isomers in solution, see ref. 7 for discussion).

Reactions of [Fe$_2$W(μ_3-CR)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)] [R = C$_6$H$_4$Me-4 (**1a**) *or* Me (**1b**)].—(*a*) *With sulphur.* (*i*) A mixture of (**1a**) (0.047 g, 0.066 mmol) and elemental sulphur (3 mg, 0.09 mmol) was dissolved in thf (10 cm^3). The dark brown mixture was stirred under a slow nitrogen gas purge for 24 h. Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane (5 cm^3), and filtered through an alumina pad (*ca.* 2 cm). Following evaporation of solvent, the residue was treated with light petroleum and cooled to give dark red *needles* of [Fe$_2$W(μ–CC$_6$H$_4$Me–4)(μ_3–S)(CO)$_7$(η–C$_5$H$_5$)] (**2**) (0.043 g).

(*ii*) A mixture of (**1b**) (0.43 g, 0.67 mmol) and sulphur (0.11 g, 3.43 mmol) in thf (40 cm^3) was stirred at room temperature for 2 d. Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane–light petroleum (2:3) and chromatographed on Florisil. Elution with the same solvent mixture gave yellow, red, and purple bands. The first two represented trace amounts of unidentified compounds. The purple eluate was evaporated and the residue dissolved in dichloromethane (*ca.* 1 cm^3). Slow addition of light petroleum (*ca.* 10 cm^3) afforded purple *crystals* of [Fe$_2$W(μ_3–SCMe)(CO)$_8$(η–C$_5$H$_5$)] (**7**) (0.13 g).

Other reactions between (**1b**) and sulphur, under similar conditions, produced mixtures of complexes (**7**) and (**8**); the latter formed in yields of up to 30%. The two species are readily separated by column chromatography.

(*b*) *With selenium.* (*i*) A mixture of (**1a**) (0.41 g, 0.57 mmol) and selenium (0.13 g, 1.71 mmol) in thf (25 cm^3) was stirred at room temperature for several hours with only partial reaction occurring (i.r. monitoring). The mixture was then warmed to *ca.* 50 °C for 3 h to bring the reaction to completion. Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane (5 cm^3) and filtered through an alumina pad. The solution was concentrated to *ca.* 1 cm^3 and light petroleum (*ca.* 3 cm^3) added slowly to give dark red *crystals* of [Fe$_2$W(μ-CC$_6$H$_4$Me-4)(μ_3-Se)(CO)$_7$(η-C$_5$H$_5$)] (**5**) (0.29 g).

(*ii*) In a similar experiment, compound (**1b**) (0.30 g, 0.47 mmol) and selenium (0.11 g, 1.31 mmol) in warm thf (30 cm^3) for 6 h gave dark red *crystals* of [Fe$_2$W(μ-CMe)(μ_3-Se)(CO)$_7$(η-C$_5$H$_5$)] (**9**) (0.16 g).

Reactions of [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(μ-dppm)(CO)$_6$(η-C$_5$H$_5$)] (**3**).—(*a*) *With sulphur.* A mixture of compound (**3**) (0.56 g, 0.53 mmol) and sulphur (33 mg, 1.06 mmol) in thf (40 cm^3) was refluxed for 90 min. After cooling to room temperature, solvent was removed *in vacuo*, the residue dissolved in dichloromethane (10 cm^3) and filtered through a pad of alumina (3 × 2 cm). The solution was concentrated to *ca.* 1 cm^3 and light petroleum (5 cm^3) added to afford dark red *microcrystals* of [Fe$_2$W(μ-CC$_6$H$_4$Me-4)(μ-dppm)(μ_3-S)(CO)$_5$(η-C$_5$H$_5$)] (**4**) (0.34 g). ^{31}P-{^{1}H} N.m.r. (in CD$_2$Cl$_2$): δ 67.6 and 67.1 p.p.m. [AB quartet, 2 P, *J*(PP) 78 Hz].

(*b*) *With selenium.* In a similar synthesis, compound (**3**) (0.48 g, 0.45 mmol) and selenium (0.106 g, 1.35 mmol) in refluxing (3 h) thf (40 cm^3) gave dark brown *crystals*, from dichloromethane–light petroleum (1:4), of [Fe$_2$W(μ-CC$_6$H$_4$Me-4)(μ-dppm)(μ_3-Se)(CO)$_5$(η-C$_5$H$_5$)] (**6**) (0.23 g). ^{31}P-{^{1}H} N.m.r. (in CD$_2$Cl$_2$): δ 67.5 and 66.6 [AB quartet, 2 P, *J*(PP) 81 Hz].

Crystal Structure Determination of [Fe$_2$W(μ-CC$_6$H$_4$Me-4)(μ_3-S)(CO)$_7$(η-C$_5$H$_5$)] (**2**).—Crystals of (**2**) were grown from dichloromethane–light petroleum as red prisms. Diffracted intensities were collected at 298 K from a crystal of dimensions *ca.* 0.42 × 0.35 × 0.30 mm. Data were collected on a Nicolet *P*3*m* four-circle diffractometer using ω-scans. Of the total 2 216 intensities collected to $2\theta \leqslant 40°$, 1 649 had $F \geqslant 5.0\sigma(F)$, where $\sigma(F)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure, after the data had been corrected for Lorentz, polarisation, and *X*-ray absorption effects. The last was by a semi-empirical method based on azimuthal scan data.[18]

Crystal data. C$_{20}$H$_{12}$Fe$_2$O$_7$SW, M = 691.9, monoclinic, a = 9.687(9), b = 24.112(10), c = 12.491(9) Å, β = 130.41(4)°, U = 2 222(2) Å^3, Z = 4, D_c = 2.07 g cm^{-3}, F(000) = 1 320, space group $P2_1/c$, Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 67.0 cm^{-1}.

The structure was solved, and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. Hydrogen atoms were not included in the refinement. The cyclopentadienyl and tolyl ring systems were treated as rigid groups [C–C (η-C$_5$H$_5$) 1.420, C–C (aryl) 1.395 Å] the constituent atoms being given isotropic thermal parameters. All remaining atoms were given anisotropic thermal parameters. Refinement by blocked-cascade least squares led to R = 0.047 (R' = 0.050), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks > 1.5 e Å^{-3}. Scattering factors were from ref. 19. All computations were carried out on an Eclipse (Data General) computer with the SHELXTL system of programs.[18]

Crystal Structure Determination of [Fe$_2$W(μ_3-SCMe)(CO)$_8$(η-C$_5$H$_5$)] (**7**).—Conditions were as described above for (**2**), except for the following differences. A purple crystal of dimensions *ca.* 0.32 × 0.28 × 0.28 mm was used with well developed faces of the type <100>, <010>, and <001>. A total of 3 540 independent intensities were collected to $2\theta \leqslant 50°$, of these 2 568 had $F \geqslant 5\sigma(F)$. An analytical absorption correction was applied.[18]

Crystal data. C$_{15}$H$_8$Fe$_2$O$_8$SW, M = 643.6, monoclinic, a = 8.633(2), b = 14.754(5), c = 14.274(6) Å, β = 99.13(3)°, U = 1 795(1) Å^3, Z = 4, D_c = 2.38 g cm^{-3}, F(000) = 1 216, space group $P2_1/n$ (non-standard setting of $P2_1/c$), μ(Mo-K_α) = 82.8 cm^{-1}.

The structure solution and refinement was as described for (**2**), except that no constraints were applied to the cyclopentadienyl ring and all non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms were included in calculated positions. Cyclopentadienyl hydrogen atoms were given isotropic temperature factors 1.2 times those of their parent carbon atoms whilst the methyl hydrogen atoms were given a common refined isotropic thermal parameter. Refinement converged at R = 0.034 (R' = 0.036) with the weighting scheme $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$. The final electron-density difference synthesis showed no peaks > 1.2 e Å^{-3}. Atomic co-ordinates for (**2**) and (**7**) are given in Tables 5 and 6, respectively.

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