

Transition metal-substituted paraffins: synthesis and properties of some μ -saturated heterobimetallic complexes containing Mo and W or Fe and the crystal structures of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PPh}_3)\text{Mo}(\text{CH}_2)_3\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$

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Abstract

The new heterobimetallic complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{W}(\text{CH}_2)_n\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ $n = 3$ to 6; $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{W}(\text{CH}_2)_n\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ $n = 3, 4$; $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{W}(\text{CH}_2)_n\text{Mo}(\text{CO})_2(\text{PPh}_i\text{Me}_{3-i})(\eta^5\text{-C}_5\text{H}_5)]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{Mo}(\text{CO})_2(\text{PPh}_i\text{Me}_{3-i})(\eta^5\text{-C}_5\text{H}_5)]$ ($n = 3, 4$ and $i = 0$ to 3) were synthesized by direct displacement of the iodide of a metallo-iodoalkyl complex with the appropriate anion. The complexes have been fully characterised by IR, ¹H NMR, ¹³C NMR, COSY, HETCOR, HSQC and elemental analyses. X-ray diffraction studies were done on the complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PPh}_3)\text{Mo}(\text{CH}_2)_3\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$. Both compounds form monoclinic crystals in the space group $P2_1/c$. The former has a W–C(alkyl) bond length of 2.316(7) Å and Mo–C(alkyl) bond length of 2.357(7) Å and the latter a Mo–C(alkyl) bond length of 2.374(2) Å and Fe–C(alkyl) bond length of 2.076(2) Å.

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1. Introduction

These transition metal-substituted paraffins are compounds in which the paraffin chains bridge two different transition metal centres. They have the general formula $[\text{L}_x\text{M}\{(\text{CH}_2)_n\}\text{M}'\text{L}_y]$; $\text{M} \neq \text{M}'$; $n \geq 1$; L_xM , $\text{M}'\text{L}_y$ = transition metal and its associated ligands. The nature of heterodinuclear complexes, that they are mixed metallic, containing two or more adjacent metal centres, could add some other chemical dimension over those containing a single metal; not only can the metals act independently but they can also act in a cooperative manner leading to

chemistry that differs appreciably from that displayed by the single metal-containing counterparts. The possibility of metals influencing one another at close proximity has been acknowledged because different metals possess different properties [1]. The stability and electronic properties of heterodinuclear compounds may also be influenced when additional ligands with π -backbonding properties are incorporated. Such complexes, but with conjugated bridges, could also act as molecular wires or switches [2,3]. Heterodinuclear compounds can also find application in the area of organic syntheses [4]. Furthermore, the synthesis and reactivity of heterodinuclear transition metal complexes continues to attract considerable interest because of their envisaged catalytic superiority over their homobimetallic analogues [4].

These metal-substituted paraffin compounds could be good catalyst precursors or model compounds for

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catalytic intermediates or act as catalysts themselves. They have been proposed to be good models for the Fischer–Tropsch processes [5]. Bimetallic compounds with direct metal–metal bonds are reported to be commonly synthesized by a metathesis of a halide ligand, usually on a group 4 metal, with an organometallic anion, such as $[\text{Cp}(\text{CO})_2\text{M}]^-$ ($\text{M} = \text{Fe}, \text{Ru}$, $\text{Cp} = (\eta^5\text{-C}_5\text{H}_5)$) [6–10] or $[(\text{CO})_4\text{M}]^-$ ($\text{M} = \text{Co}, \text{Rh}$) [6,7,11–15]. The same procedure has been used to prepare heterobimetallic lanthanide [11] and group 6 and 9 complexes [12,13]. The most successful route to heterodinuclear alkyl bridged compounds reported so far is via the use of halogenoalkyl compounds, especially those with the iodoalkyl group [2,16,17].

Whilst a number of homometallic complexes incorporating polymethylene bridges (also called alkanediyl bridges or bridging alkyl chains) are known [17,18] and most are well covered in a recent review [19], very few heterobimetallic complexes of the type $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3\text{M}(\text{CH}_2)_n\text{M}'(\text{CO})_x(\text{L})(\eta^5\text{-C}_5\text{R}_5)]$ ($\text{M} \neq \text{M}'$, $x > 1$, $n \geq 2$) have been reported [1,2,17,18] and to our knowledge none with phosphine ligands. Only phosphine acyl complexes resulting from migratory insertion reactions have been reported [1,16,20,21]. We now report on new metal-substituted paraffin compounds containing tertiary phosphine ligands prepared from a range of previously reported halogenoalkyl compounds [22].

2. Results and discussions

The new heterodinuclear complexes were obtained in medium to high yields by the direct displacement of the iodide of a metallo-iodoalkyl complex with an appropriate anion, as shown in Scheme 1:

A $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_n\text{Mo}(\text{CO})_3\text{Cp}]$	$n = 3$ 1a
	$n = 4$ 1b
	$n = 5$ 1c
	$n = 6$ 1d
B $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_n\text{Mo}(\text{CO})_3\text{Cp}^*]$ { $\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$ }	$n = 3$ 2a
	$n = 4$ 2b
C $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_n\text{Mo}(\text{CO})_2\text{LCp}]$	
L = PPh_3	$n = 3$ 3a
	$n = 4$ 3b
L = PPh_2Me	$n = 3$ 4a
	$n = 4$ 4b
L = PPhMe_2	$n = 3$ 5a
	$n = 4$ 5b
L = PMe_3	$n = 3$ 6a
	$n = 4$ 6b
D $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{Mo}(\text{CO})_2\text{LCp}]$	
L = PPh_3	$n = 3$ 7a
	$n = 4$ 7b

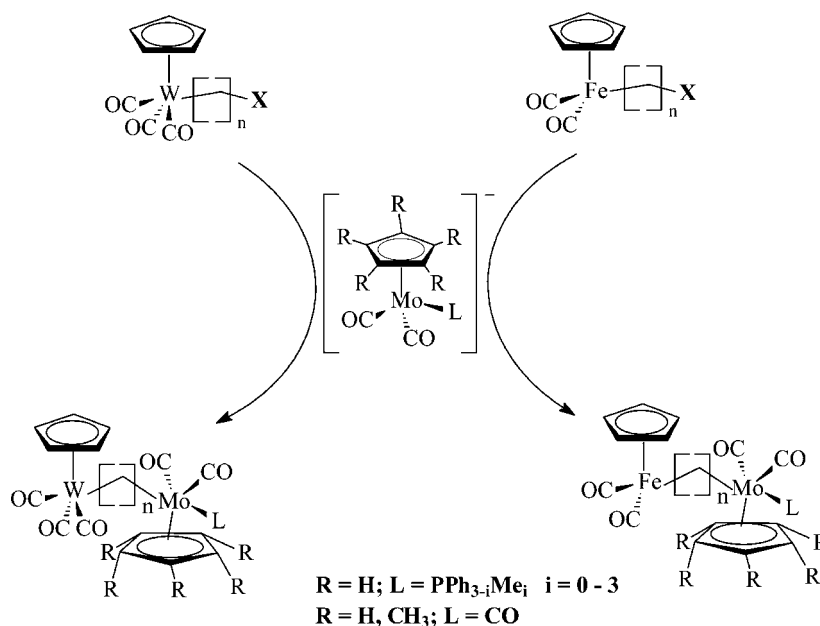
L = PPh_2Me	$n = 3$ 8a
	$n = 4$ 8b
L = PPhMe_2	$n = 3$ 9a
	$n = 4$ 9b
L = PMe_3	$n = 3$ 10a
	$n = 4$ 10b
E $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{Mo}(\text{CO})_3\text{Cp}^*]$	$n = 3$ 11a
	$n = 4$ 11b

The compounds of type **A** were obtained in best yields when the temperature of the reactions was maintained at -78 °C over the total reaction period, which ranged from 64 to 105 h. Compounds of class **B** were prepared in an analogous manner to class **A** and were also obtained in good yields. The reactions were found to take a shorter time when carried out at room temperature, however, the yields were low and this was attributed to a high decomposition rate of the reactants. The reactions using the phosphine-substituted anions to yield class **C** and **D** compounds were slow but gave good yields at room temperature. The reaction times generally increased with an increase in chain length. This could be attributed to decreased influence of the metal on the halogen within the same molecule.

The complexes of class **A**, **B** and **E** were soluble in hexane with their solubility increasing with increasing length of the alkyl chain. The rest of the complexes were insoluble in hexane due to the presence of the phosphine ligand, but soluble in dichloromethane. All the complexes were obtained as yellow crystalline solids, which were stable in air but unstable in solution.

The melting points were generally sharp and decreased with increase in alkyl chain length. The notable exceptions are compounds **4** and **10**. The yields, spectral data and melting points are given in Table 1.

In the IR spectra, the $\nu(\text{CO})$ wave numbers of the complexes are in the expected range for terminal carbonyl groups [17]. Some of the $\text{W}(\text{CO})$ or $\text{Fe}(\text{CO})$ and $\text{Mo}(\text{CO})$ peaks overlap, but the peaks between 1830 and 1850 cm^{-1} can be clearly assigned to $\text{Mo}(\text{CO})$ [1,17]. Steric effects of the phosphines are difficult to separate from electronic factors and hence are closely interrelated [23,24]. Since PMe_3 is the most basic phosphine within the group with the lowest π -acceptor properties, its complexes have the strongest $\text{M}(\text{CO})$ bonds and hence the lowest frequency infrared bands in the $\nu(\text{CO})$ region. A decreasing trend is thus expected in the carbonyl stretching frequencies as phenyl groups are sequentially substituted by methyl groups in the phosphine ligands used. This trend is evident for the $\text{Mo}(\text{CO})$ bands between 1830 and 1850 cm^{-1} for compounds of class **C** and **D** where $n = 4$, but not where $n = 3$, presumably due to the influence of the metal at the other end of the alkyl chain.



Scheme 1. The general synthetic pathway to the heterobimetallic complexes.

The 1H NMR data for the complexes **1a–11b** are summarised in Table 2. Data from similar compounds [17,22], as well as correlated spectroscopy (COSY), were used for chemical shift assignments.

A shielding effect is seen on the $MoCH_2$ protons of compounds **8a**, **9a**, **10a** and **10b** and they appear upfield relative to uncoordinated aliphatic methylene protons. Tungsten, being a more electron-rich transition metal, shields its $\alpha-CH_2$ protons more and these peaks were observed further upfield than those α to the Mo atom. The influence of the metal diminishes as the chain gets longer, and has no effect at all on the chemical shifts of the protons of either Cp or Cp*. The observations here support an earlier finding that the metal only influences the protons α and β to it and not those γ or beyond [17]. Because of these observations, compounds with longer alkyl chain length ($n = 5$ and above) were not synthesized for compounds of class **B–E**.

All the Cp proton resonances of the compounds of class **C** and **D** were observed to couple with the phosphorus of the phosphine ligands and hence the peaks for the Cp ligands were all observed as doublets. In this type of complex, it has been noted that the bulky phosphine ligand always preferentially migrates away from the approaching alkyl ligand giving a *trans* geometry with an average P–Mo–C(alkyl) angle of 135° (see Fig. 1) [22,25, this work]. We have also confirmed this observation from the crystal structures obtained for compounds **3a** and **7a** as can be seen in Figs. 2 and 3.

The ^{13}C NMR data for complexes **1a–11b** are given in Table 3. The peak assignments were made using heteronuclear correlation (HETCOR) and heteronuclear single-quantum correlation (HSQC) experiments. In

addition comparisons were made to the ^{13}C NMR data reported for related heterodinuclear complexes of Fe and Mo, W, Re and Ru [17]. The metals on the opposite end of the paraffin chain and the chain length were seen to have no effect on the chemical shifts of the carbonyl peaks. Similarly, neither the metals on the opposite end of the paraffin chain, nor the chain length appear to affect the positions of Cp* and Cp peaks significantly. These peaks for the complexes **4a–10b**, with phosphines as ligands, appear at slightly lower field, compared to the unsubstituted compounds (**1a–1d**).

The signals of carbon atoms in the carbonyl ligands *cis* to the phosphine ligand were also observed as doublets because of coupling with the phosphorus atom. Again the stereochemistry was confirmed by the crystal structures of **3a** and **7a** (Figs. 2 and 3).

From the ^{13}C NMR data in Table 3, it can be seen that the chemical shifts of the carbon α to a metal generally decreases with an increase in the bridging chain length. This suggests that an increase in the chain length results in a reduced influence of the metal at one end of the chain on the carbon α to the other metal at the other end of the chain. This is not observed for the Cp* compounds **2a** and **2b**, however. We find that the $MoCH_2$ carbon atoms in the $MoCp^*$ compounds **2** are significantly more deshielded than those of the $MoCp$ compounds. The deshielding effect is weaker on the $MoCH_2CH_2$ carbons.

The compounds **2a**, **5b** and **10a** were analysed for the presence of the elements Fe, Mo, W and combinations of FeMo and MoW by liquid chromatography time-of-flight mass spectrometry (LC-ToF-MS). Computer simulations of the expected patterns were generated by

Table 1
 Data for the compounds $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{L})\text{Mo}(\text{CH}_2)_n(\text{CO})_x(\eta^5\text{-C}_5\text{R}_5)]$; $n = 3, 4$; $\text{M} = \text{Fe}$ ($x = 2$), W ($x = 3$), $\text{R} = \text{H}$, CH_3); $\text{L} = \text{CO}$; $\text{PPh}_i\text{Me}_{3-i}$; $i = 0$ to 3 ; $n = 5, 6$; $\text{M} = \text{W}$ ($x = 3$); $\text{L} = \text{CO}$; **1a–11b**

Type	Compound	Yield (%)	m.p. (°C)	IR $\nu(\text{CO})$ (cm^{-1})
A	1a	78	171–175(>, dec)	1966s
	1b	96	>145(dec)	1963s
	1c	46	>95(dec)	1976s
	1d	89	>89(dec)	1963s
B	2a	51	147–150	1966s
	2b	61	119–124	1998sb
C	3a	45	95–99	1968
	3b	53	88–94	1976
	4a	94	68–70	1966
	4b	96	112–115	1971
	5a	88	116–118	1972
	5b	91	109–110	1969
	6a	66	>120(dec)	1969
	6b	73	114–115	1967
	7a	49	97–99	1938sb
	7b	74	71–78	1939vsb
D	8a	69	>124(dec)	1962sh
	8b	73	69–72	1969s
	9a	41	>138(dec)	1936sh
	9b	69	97–98	1938sb
	10a	56	90–96	1936vs
	10b	75	108–110	1938vs
	11a	49	65–68	1941s
	11b	94	71–78	1939s
E	1a	78	171–175(>, dec)	1966s
	1b	96	>145(dec)	1963s
	1c	46	>95(dec)	1976s
	1d	89	>89(dec)	1963s
	2a	51	147–150	1966s
	2b	61	119–124	1998sb
	3a	45	95–99	1968
	3b	53	88–94	1976
	4a	94	68–70	1966
	4b	96	112–115	1971
	5a	88	116–118	1972
	5b	91	109–110	1969
6a	66	>120(dec)	1969	
6b	73	114–115	1967	
7a	49	97–99	1938sb	
7b	74	71–78	1939vsb	
8a	69	>124(dec)	1962sh	
8b	73	69–72	1969s	
9a	41	>138(dec)	1936sh	
9b	69	97–98	1938sb	
10a	56	90–96	1936vs	
10b	75	108–110	1938vs	
11a	49	65–68	1941s	
11b	94	71–78	1939s	

vs = very strong, s = strong, b = broad, sh = shoulder.

^a In hexane.

^b In dichloromethane.

Table 2
¹H NMR data for $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{L})\text{Mo}(\text{CH}_2)_n\text{M}(\text{CO})_x(\eta^5\text{-C}_5\text{R}_2)]^{\beta}$; $n = 3, 4$; $\text{M} = \text{Fe}$ ($x = 2$), W ($x = 3$, $\text{R} = \text{H}, \text{CH}_3$); $\text{L} = \text{CO}$; PPh_3 ; $\text{Me}_3\text{-}i = 0$ to 3 ; $n = 5, 6$; $\text{M} = \text{W}$ ($x = 3$); $\text{L} = \text{CO}$; **1a–11b**

Type	Compound	CpMo	C ₅ (CH ₃) ₅ Mo	Cp'	α-Mo	α-M'	β-Mo	β-M'	γ-Mo	γ-W	P-Ph	P-CH ₃
A	1a	5.27s		5.36s	1.58m	1.53m	1.83s					
	1b	5.25s		5.35s	1.59s	0.86s	1.83s	1.55s				
	1c	5.26s		5.35s	1.58s	1.32s	1.84s	1.57s	1.82s			
	1d	5.25s		5.40s	1.51s	1.23s	1.83s	1.56s	1.81s	1.76s		
B	2a		1.85s	5.36s	1.67m	0.99m	1.63m					
	2b		1.85s	5.35s	1.65s	0.85s	1.58s	1.23s				
C	3a	4.73s		5.36s	1.68m	1.29m	1.62m				7.36s, 15H	
	3b	4.70s		5.35s	1.63s	0.83s	1.54s	1.23s			7.37s, 15H	
	4a	4.96s		5.39s	1.66s	1.24s	1.48s				7.36m, 10H	2.10d, 8.9 ^b , 3H
	4b	4.69s		5.35s	1.62s	0.89s	1.49s	1.23s			7.36m, 10H	2.07d, 8.8, 3H
	5a	4.72s		5.37s	1.65s	1.22s	1.45s				7.37m, 5H	1.82d, 8.2, 6H
	5b	4.70s		5.35s	1.61s	0.89s	1.47s	1.24s			7.37m, 5H	1.82d, 8.2, 6H
D	6a	4.88s		5.38s	1.64s	1.23s	1.47s				1.49d, 8.8, 9H	
	6b	4.87s		5.34s	1.66s	0.83s	1.46s	1.23s			1.49d, 8.9, 9H	
E	7a	4.71s		4.72s	1.63m	1.23m	1.52m				7.36m, 15H	
	7b	4.70s		4.70s	1.66s	0.84s	1.53s	1.23s			7.36m, 15H	
	8a	4.71s		4.70s	1.24s	1.48s	1.76s				7.37m, 10H	2.07d, 8.9, 3H
	8b	4.95s		4.70s	1.62s	0.85s	1.49s	1.23s			7.37m, 10H	2.15d, 8.9, 3H
	9a	4.94s		4.71s	1.23s	1.48s	1.79s				7.39m, 5H	2.00d, 8.2, 6H
	9b	4.94s		4.70s	1.62s	0.85s	1.42s	1.23s			7.40m, 5H	2.05d, 8.2, 6H
	10a	4.88s		4.71s	1.35s	1.43s	1.69s				1.48d, 10.4, 9H	
	10b	4.88s		4.69s	1.34s	1.42s	1.66s				1.48d, 8.9, 9H	
	11a		1.85s	4.70s	1.64m	1.23m	1.46m					
	11b		1.84s	4.70s	1.61s	0.96s	1.58s	1.46s				

^aIn CDCl₃ relative to TMS (0.00 ppm).^bJ values are given in Hz. M' = Fe or W. Cp' = Cp on either Fe or W. β-Mo refers to the carbon atom of the alkyl chain β to Mo etc.

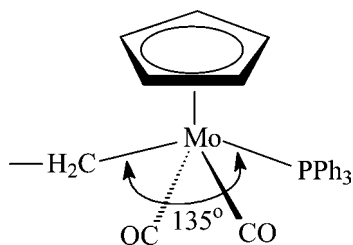
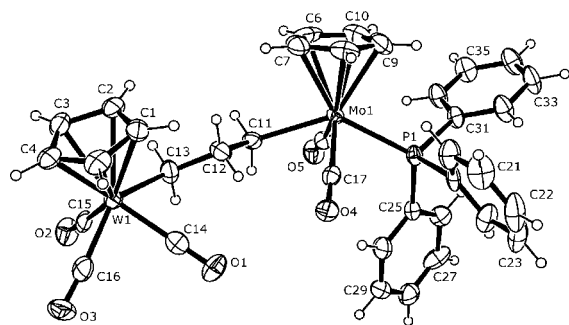
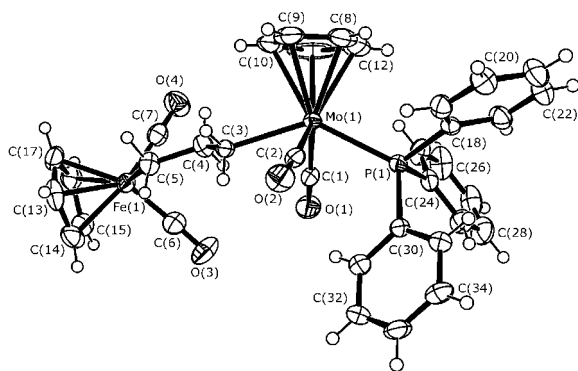


Fig. 1. The P–Mo–C angle.

Fig. 2. The molecule of **3a**, showing the atom-labelling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms as spheres of arbitrary radius.Fig. 3. The molecule of **7a**, showing the atom-labelling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms as spheres of arbitrary radius.

using (NIST) “Isoform” computer software [26]. The spectrum of compound **2a** with the molecular formula $C_{24}H_{26}MoO_6W$, showed large ions present at m/z 715.0150 corresponding to $[M + Na]^+$, a “pseudo-molecular ion” that is usually generated by electrospray ionization. The predicted isotope distribution pattern resembled the experimental finding; for compound **5b**, both the isotope abundance pattern and the accurate mass (measured 788.0599, calculated 788.0660, difference 7.7 ppm) corresponded to the “pseudo-molecular ion” $[M + CH_3CN + H]^+$. The cluster ion incorporated a molecule of the acetonitrile used as solvent hence the mass occurred at 42 mass units higher than expected (it should be noted that this phenomenon is not unusual in

this type of analysis), for compound **10a**, $C_{20}H_{25}FeMoO_4P$, the mass spectrum obtained showed the isotope ratio pattern of the most intense cluster around m/z 556, again 42 mass units higher than expected, also implying a “pseudo-molecular ion” of the formula $[M + CH_3CN + H]^+$.

2.1. Crystal structures of compounds **3a** and **7a**

Only structures of homodinuclear alkanediyl compounds are reported in the literature and, to our knowledge, none with two different metals present in the same molecule [27–30]. Archer et al. reported only the severely disordered $[Cp(CO)_2Fe(CH_2)_6Ru(CO)_2Cp]$ [5]. We have recently reported the structure of the heterobimetallic compound $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ which showed a partial (24%) disorder by inter-change of Fe and Ru that renders the bonds to Fe and Ru apparently slightly longer and shorter, respectively, than they are in the corresponding homodinuclear analogues [31]. The compounds $[Cp(CO)_3W(CH_2)_3Mo(CO)_2(PPh_3)Cp]$ (**3a**) and $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_2(PPh_3)Cp]$ (**7a**), discussed below are therefore, to our knowledge, the first ordered crystal structures of heterodinuclear alkanediyl compounds in general, and the first for Mo and Fe or W.

The molecules of **3a** and **7a** are shown in Figs. 2 and 3, respectively. Selected bond lengths and angles and details of data collection and structure refinement are given, in each case for both compounds together, in Tables 4 and 5, respectively. In Table 4, the contribution of the pentahapto cyclopentadienyl ligand to the coordination of the metal atoms is expressed, for convenience and brevity, in terms of a single bond to its centroid (Cg). The bond lengths and angles of the triphenylphosphine, cyclopentadienyl and carbonyl ligands are in no way unusual, e.g., carbonyl C–O distances and M–C–O angles in the respective ranges 1.145(3)–1.154(3) Å and 175.2(5)–178.4(6)°, and are not discussed in detail here but are available in the cif supplementary data deposited with CCDC. Instead the discussion here concentrates upon the molybdenum, tungsten and iron moieties and, because there is no structure similar to that of **3a** or **7a** in the literature, compares them with some reported but not wholly analogous structures [22].

In compounds **3a** and **7a**, as expected, the PPh_3 ligand on the molybdenum atom is *trans*, and the carbonyl groups and the cyclopentadienyl ligands are *cis*, to the alkyl chain. Conversely the Cp and the CO ligands on the molybdenum centre are *cis* to the PPh_3 . This confirms the ^{13}C NMR interpretations that showed doublets for the two carbonyl ligands as a result of coupling with the phosphorus atom. The ligands are disposed in a piano stool fashion, which can also be regarded as being in the form of a square pyramid with the cyclopentadienyl li-

Table 3
 ^{13}C NMR data for $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{L})\text{Mo}(\text{CH}_2)_n\text{M}(\text{CO})_x(\eta^5\text{-C}_5\text{R}_5)]^{\text{M}}$; $n = 3, 4$; $\text{M} = \text{Fe}$ ($x = 2$), W ($x = 3$, $\text{R} = \text{H}$, CH_3); $\text{L} = \text{CO}$; PPh_2Me_3 ; $i = 0$ to 3 ; $n = 5, 6$; $\text{M} = \text{W}$ ($x = 3$); $\text{L} = \text{CO}$; **1a–11b**

Type/Cpd	MoCO	$\text{M}^{\text{CO}}_{(\text{cis})}$ ^b	$\text{M}^{\text{CO}}_{(\text{trans})}$ ^b	CpMo	Cp*(C)	Cp*(CH ₃)	CpM'	α -Mo	α -M'	β -M' ^c	β -Mo ^d	γ -W	γ -Mo	Ph	P-Me
A															
1a	217s	227s	239	92.6s			91.4s	7.6s	-5.1s	44.3s					
1b	217s	227s	<i>f</i>	92.9s			91.7s	2.4s	-10.1s	43.2s	25.8s				
1c	218s	227s	<i>f</i>	93.7s			92.5s	3.8s	<i>f</i>	37.6s	26.6s	36.7s			
1d	217s	227s	240s	92.7s			91.4s	2.7s	-9.8s	36.8s ^e	14.1s	36.4s ^e	25.6s		
B															
2a	217s	231s	240s		104.02s	10.36s	91.33s	18.48s	-3.62s	43.71s					
2b	217s	231s	<i>f</i>		104.15s	10.32s	91.51s	20.80s	-9.99s	43.82s ^e	40.41s ^e				
C															
3a	<i>f</i>	229s	217s	92.50s			91.49s	1.02s	-3.69s	44.51s				128d, 10.0	
3b	<i>f</i>	229s	217s	92.67s			91.72s	3.72s	-9.47s	43.80s	42.45s			128d, 9.7	
4a	237d, 22.6	229s	217s	92.22s			91.41s	17.05s	-3.69s	44.67s				128d, 9.7	21.61d, 34.8
4b	237d, 22.6	229s	217s	91.76s			91.53s	2.55s	-9.39s	43.80s	43.14s			128d, 9.6	21.02d, 34.4
5a	237d, 22.7	228s	217s	91.62s			91.38s	8.61s	-3.61s	44.72s				128d, 9.6	21.00d, 32.9
5b	236d, 22.6	229s	217s	91.74s			91.49s	2.67s	-9.42s	43.78s	43.12s			128d, 9.7	17.59d, 31.9
6a	238d, 22.8	229s	217s	91.81s			91.37s	10.47s	-11.97s	44.57s				128d, 9.7	22.22d, 32.8
6b	238d, 22.6	229s	217s	91.51s			90.95s	1.92s	-9.35s	43.93s ^e	43.31s ^e				
D															
7a	238d, 32.0	<i>f</i>	218s	92.51s			85.20s	9.46s	7.79s	43.03s				128d, 9.7	
7b	238d, 34.0	<i>f</i>	218s	92.87s			85.57s	4.61s	4.22s	45.41s	41.66s			128d, 9.7	
8a	236d, 34.1	<i>f</i>	217s	92.23s			85.18s	8.05s	9.45s	45.83s				127d, 9.6	21.15d, 34.3
8b	234d, 34.0	<i>f</i>	<i>f</i>	92.33s		85.58s	0.99s	14.09s	31.56s	22.63s				128d, 9.7	20.80d, 34.5
9a	234s	<i>f</i>	217s	91.66s			85.17s	7.57s	9.51s	45.95s				128d, 9.6	21.02d, 32.9
9b	237s	<i>f</i>	217s	91.96s			87.95s	3.32s	8.63s	41.75s	37.45s			128d, 9.6	18.50d, 32.4
10a	236s	<i>f</i>	217s	90.85s			85.16s	6.80s	9.60s	46.10s				128d, 9.6	21.84d, 29.8
10b	236s	<i>f</i>	217s	90.93s			85.31s	2.23s	4.05s	45.25s	42.35s				21.83d, 32.1
E															
11a	<i>f</i>	230s	218s		103.98s	11.8s	85.7s	1.5s	8.2s	47.4s					
11b	<i>f</i>	231s	217s		104.12s	10.4s	85.4s	3.6s	10.3s	45.4s	41.1s				

^a Measured in CDCl_3 relative to TMS ($\delta = 0.00$ ppm).

^b Relative the alkyl chain.

^c β -M' refers to the carbon atom of the alkyl chain β to M'.

^d β -Mo refers to the carbon atom of the alkyl chain β to Mo etc.

^e Assignments could be interchanges. *f*, Not observed. Cp' = Cp on either Fe or W. M' refers to either W or Fe.

Table 4
Selected bond lengths and angles (Å, °) for **3a** and **7a**

	3a: M = W		7a: M = Mo		7a: M = Fe		
<i>Apical X</i>							
Mo(1)–Cg(1)	2.022(4)	W(1)–Cg(2)	1.997(3)	Mo(1)–Cg(3)	2.0164(16)	Fe(1)–Cg(4)	1.7206(15)
<i>Basal Y</i>							
Mo(1)–C(17)	1.960(7)	W(1)–C(14)	1.988(8)	Mo(1)–C(1)	1.954(3)	Fe(1)–C(6)	1.748(3)
Mo(1)–C(18)	1.957(7)	W(1)–C(15)	1.967(7)	Mo(1)–C(2)	1.949(3)	Fe(1)–C(7)	1.745(3)
Mo(1)–C(11)	2.357(7)	W(1)–C(16)	1.984(8)	Mo(1)–C(3)	2.374(2)	Fe(1)–C(5)	2.076(2)
Mo(1)–P(1)	2.4569(17)	W(1)–C(13)	2.316(7)	Mo(1)–P(1)	2.4546(10)		
<i>Alkane</i>							
C(11)–C(12)	1.527(9)	C(12)–C(13)	1.519(9)	C(3)–C(4)	1.488(3)	C(4)–C(5)	1.522(4)
<i>X–M–Y</i>							
Cg(1)–Mo(1)–C(17)	129.9(2)	Cg(2)–W(1)–C(14)	125.9(2)	Cg(3)–Mo(1)–C(1)	131.80(9)	Cg(4)–Fe(1)–C(6)	124.32(11)
Cg(1)–Mo(1)–C(18)	125.1(2)	Cg(2)–W(1)–C(15)	128.0(2)	Cg(3)–Mo(1)–C(2)	125.03(10)	Cg(4)–Fe(1)–C(7)	127.20(11)
Cg(1)–Mo(1)–C(11)	108.32(19)	Cg(2)–W(1)–C(16)	117.5(2)	Cg(3)–Mo(1)–C(3)	108.17(8)	Cg(4)–Fe(1)–C(5)	122.47(10)
Cg(1)–Mo(1)–P(1)	116.54(13)	Cg(2)–W(1)–C(13)	108.8(2)	Cg(3)–Mo(1)–P(1)	115.97(6)		
<i>Adjacent Y</i>							
C(17)–Mo(1)–C(11)	74.5(2)	C(14)–W(1)–C(16)	77.7(3)	C(1)–Mo(1)–C(3)	71.93(9)	C(6)–Fe(1)–C(7)	97.01(13)
C(17)–Mo(1)–P(1)	78.00(18)	C(14)–W(1)–C(13)	75.0(3)	C(1)–Mo(1)–P(1)	77.34(7)	C(5)–Fe(1)–C(6)	84.72(11)
C(18)–Mo(1)–C(11)	72.5(2)	C(15)–W(1)–C(16)	77.8(3)	C(2)–Mo(1)–C(3)	73.64(9)	C(5)–Fe(1)–C(7)	89.27(11)
C(18)–Mo(1)–P(1)	80.60(18)	C(15)–W(1)–C(13)	74.4(3)	C(2)–Mo(1)–P(1)	82.68(8)		
<i>Diag. opp. Y</i>							
C(17)–Mo(1)–C(18)	103.8(3)	C(14)–W(1)–C(15)	105.5(3)	C(1)–Mo(1)–C(2)	101.80(10)		
C(11)–Mo(1)–P(1)	135.12(17)	C(13)–W(1)–C(16)	133.7(3)	C(3)–Mo(1)–P(1)	135.83(6)		
<i>Alkane</i>							
Mo(1)–C(11)–C(12)	120.1(2)	C(12)–C(13)–W(1)	116.4(5)	Mo(1)–C(3)–C(4)	118.20(15)	C(4)–C(5)–Fe(1)	116.93(17)
C(11)–C(12)–C(13)	110.1(6)			C(3)–C(4)–C(5)	112.4(2)		

Table 5
Crystal data and structure refinement for **3a** and **7a**

	3a : M = Mo and W	7a : M = Mo and Fe
Empirical formula	C ₃₆ H ₃₁ MoO ₅ PW	C ₃₅ H ₃₁ FeMoO ₄ P
Molecular weight	854.37	698.36
Temperature (K)	219(2)	228(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimension		
<i>a</i> (Å)	15.446(7)	15.414(7)
<i>b</i> (Å)	12.204(6)	11.243(4)
<i>c</i> (Å)	18.483(9)	19.007(6)
β (°)	113.27(4)	112.42(3)
<i>Z</i>	4	4
<i>D</i> _{calc} (mg m ⁻³)	1.773	1.523
Absorption coefficient (mm ⁻¹)	4.075	0.979
<i>F</i> (000)	1672	1424
Crystal colour	Yellow	Yellow
Crystal size (mm)	0.45 × 0.35 × 0.25	0.45 × 0.40 × 0.30
θ Range for data collection (°)	2.06–23.01	2.15–23.00
Index range	–15 ≤ <i>h</i> ≤ 16 –13 ≤ <i>k</i> ≤ 13 –20 ≤ <i>l</i> ≤ 0	–15 ≤ <i>h</i> ≤ 16 –12 ≤ <i>k</i> ≤ 12 –20 ≤ <i>l</i> ≤ 0
Reflections collected/unique [<i>R</i> _{int}]	8643/4452 [0.0448]	8177/4230 [0.0187]
Completeness to θ limit (%)	99.5	99.6
Absorption correction	Refine Δ(<i>F</i> ²) (DIFABS)	Refine Δ(<i>F</i> ²) (DIFABS)
Max. and min. transmission	0.4290 and 0.2614	0.7578 and 0.6671
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4452/0/397	4230/0/379
Goodness-of-fit on <i>F</i> ²	1.038	1.023
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] <i>R</i> ₁	0.0360	0.0214
<i>wR</i> ₂	0.0989	0.0545
<i>R</i> indices (all data) <i>R</i> ₁	0.0421	0.0296
<i>wR</i> ₂	0.1033	0.0570
Largest diff. peak and hole (e Å ⁻³)	1.403 and –1.821	0.327 and –0.297

gand at the apex, similar to some reported complexes with analogous features [32]. Very few molybdenum–alkyl structures are known and to date those with the Cp(CO)₂(PR₃) ligand pattern have only recently been reported by us [22]. In **3a** and **7a**, the Mo(1)–C_{alkyl} bond lengths are 2.357(7) and 2.374(2) Å, within the general range (2.26–2.38 Å) of the few reported molybdenum–alkyl structures [22,28] including 2.402(7) Å reported for [Cp(CO)₃Mo{(CH₂)₃I}]. The Mo(1)–P(1) bond lengths [2.4569(17) and 2.4546(10) Å] are likewise in the normal range (2.41–2.51 Å) [33–37]. The Mo–C_{Cp} distances range from 2.322(7) to 2.370(7) Å.

In compound **3a**, the W–C_{Cp} distances range from 2.315(7) to 2.349(7) Å. The carbonyl ligands have W–C–O angles ranging from 176.1(8) to 179.0(7). The C–O bond lengths of between 1.146(10) and 1.16(11) Å, and the mean W–C(CO) bond length of 1.97 Å are normal for terminal carbonyl groups. The W–C(sp³) bond distance of 2.316(7) Å is significantly longer than that of the recently reported monometallic halogenoalkyl compound [Cp(CO)₃W{(CH₂)₅I}] 2.08(3) Å [22] but is in the range of a methyl group bound to a d⁴-tungsten center [38–40].

The situation of the iron atom in **7a** is rather different from that described for molybdenum and tungsten. The ligands are now disposed in the form of a trigonal pyramid, or three legged stool, with the cyclopentadienyl ligand at the apex. A direct consequence of this is that the Cp on the iron centre is roughly perpendicular to the alkyl chain and at an angle of 74.27(17)° to the Cp associated with molybdenum whereas in **3a** the Cp's associated with molybdenum and tungsten are both on the same side of and roughly parallel to the alkyl chain and make an angle of only 25.0(5)° to one another. The projection of the Cp(CO)₂Fe-unit of the compound, [Cp(CO)₂Fe(CH₂)₃Fe(CO)₂Cp], though homobimetallic, shows, also in contrast to **7a**, the cyclopentadienyl ring near parallel to the alkyl chain [28]. This suggests that this is the energetically favoured extended staggered conformation for this molecule, a phenomenon also observed for the compound [Cp*(CO)₂Fe(C₅H₁₁)] [41]. The Fe(1)–C(5) bond length to the alkyl chain in **7a** is 2.076(2) Å, in the general range of reported Fe–C bonds (2.05–2.08 Å) [25,28,42–46] and the Fe–C_{Cp} distances range from 2.088(3) to 2.102(3) Å. The compound follows the typical ‘bump in hollow’ packing, as is often

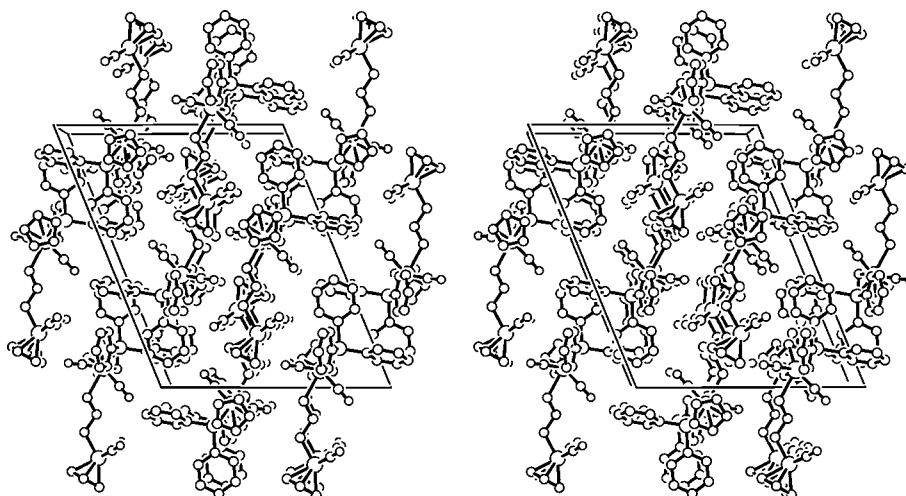


Fig. 4. The unit cell of **7a** viewed down the crystallographic *a*-axis (100 projection). Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms have been omitted for clarity.

observed in the packing of paraffinic molecules (Fig. 4) [39]. The C–C bond lengths in the alkyl chains are within the general range observed in the similar compounds referred to above (1.48–1.55 Å).

We are presently investigating the chemistry of these compounds and hope to publish these results in the near future.

3. Experimental

All reactions were carried out under inert conditions using standard Schlenk tube techniques. The dimers $[\text{Cp}(\text{CO})_3\text{Mo}]_2$, $[\text{Cp}^*(\text{CO})_3\text{Mo}]_2$, $[\text{Cp}(\text{CO})_2\text{Mo}(\text{PPh}_i\text{Me}_3\text{-}i)]_2$ and the halogenoalkyl compounds, $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{I}\}]$, were made according to the literature [22]. The dicyclopentadiene was always distilled prior to use. Tetrahydrofuran was distilled over sodium-benzophenone and stored over sodium wire. Dichloromethane and chloroform were purified according to the literature procedure and stored over molecular sieves 3 Å under nitrogen [46]. The molecular sieves 3 and 4 Å were dried in a tube furnace at 250 °C for 10 h and alumina was deactivated with deionised water and dried in an oven at 110 °C before use. Melting points were recorded on a Kofler hot-stage microscope and are uncorrected. The South African Bureau of Standards (SABS) in Richards Bay, South Africa performed the elemental analyses. Infrared spectra were recorded on a Nicolet Impact 400D 5DX FT-spectrophotometer either in solution or KBr disc. The NMR spectra were recorded on Varian Gemini 300 MHz and Varian Inova 400 spectrometers. X-ray diffraction studies were carried out using an Enraf-Nonius CAD4 diffractometer in the Chemistry Department of our Pietermaritzberg campus. LC-ToF-MS data were obtained on a Jaguar LC-TOF-MS at the

LECO Corporation Separation Science Laboratory in the United States. All reactions were followed by IR, by monitoring the disappearance of the $\nu(\text{CO})$ peaks of the anions.

3.1. Preparation of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_3\text{Cp}]$

A solution of the salt $\text{Na}[\text{Cp}(\text{CO})_3\text{Mo}]$ was prepared by the reduction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ (0.88 g 1.80 mmol), by an amalgam made from Na (0.25 g, 10.8 mmol) and mercury (6 ml), in tetrahydrofuran (25 ml). The resulting solution was added dropwise over 30 min to a stirred solution of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{I}\}]$ (1.80 g, 3.6 mmol) dissolved in THF (6 ml) and maintained at –78 °C. The solution obtained was maintained between –65 and –78 °C. After 64 h, no infrared bands due to the anion $[\text{Cp}(\text{CO})_3\text{Mo}]^-$ were observed. The mixture was, however, stirred for a further 12 h to ensure complete reaction, after which it was filtered through a cannula under nitrogen. The solvent was removed under reduced pressure and the residue dissolved in a minimum amount of dichloromethane and transferred to a short chromatography column made up of alumina with hexane and maintained under nitrogen. Elution with hexane gave a light yellow band that was found to contain only the starting material. The second, intense, yellow band eluted was concentrated and recrystallised at –78 °C. The desired product separated from the solution. The mother liquor was syringed off and the product dried under reduced pressure.

It is also possible to avoid chromatography by four successive recrystallizations of the filtered product from a minimum of dichloromethane/hexane at –78 °C to give an analytically pure product. Elemental

Anal.: Found (Calc.): **1a** C 35.98 (36.69) H 2.77 (2.59)%.

3.2. Preparation of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_4\text{Mo}(\text{CO})_3\text{Cp}]$

An amalgam of Na/Hg, made as described above, was used to reduce the compound $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ (0.78 g, 1.59 mmol) to the anion $[\text{Cp}(\text{CO})_3\text{Mo}]^-$ (3.2 mmol) in THF (30 ml). This solution of $\text{Na}[\text{Cp}(\text{CO})_3\text{Mo}]$ was added dropwise over 30 min into a stirred solution of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{I}\}]$ (0.88 g, 1.70 mmol, 10% less than quantity of the salt) in THF (6 ml) maintained at -78°C . The reaction was maintained at this temperature for 84 h. The solution was then filtered through a cannula under nitrogen and the solvent removed under reduced pressure. The residue was dissolved in a minimum of dichloromethane. An equal volume of hexane was added and the resulting mixture cooled to -78°C . The product precipitated out, and the mother liquor was syringed off. The product was recrystallised four times from dry hexane (80 ml in total) at -78°C . Elemental Anal.: Found (Calc.): **1b** C 36.84 (37.77), H 2.87 (2.85)%.

3.3. Preparation of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_n\text{Mo}(\text{CO})_3\text{Cp}]$ $n = 5, 6$

The same reaction conditions and work-up procedures were used as for **1b** above, except that the reactants, once mixed, were kept at -78°C for 24 h and then allowed to attain room temperature and stirred for a further 5 days.

3.4. Preparation of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_n\text{Mo}(\text{CO})_3\text{Cp}^*]$ $n = 3, 4$

The salt $\text{Na}[\text{Cp}^*\text{Mo}(\text{CO})_3]$ was prepared by reducing $[\text{Cp}^*\text{Mo}(\text{CO})_3]_2$ (0.152 g, 0.242 mmol) with Na (0.25 g, 10.8 mmol)/Hg (6 ml) in THF (25 ml). The solution was added dropwise over a period of 30 min to a stirred solution of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{I}\}]$ (0.242 g, 0.484 mmol) dissolved in THF (5 ml) and maintained at -78°C . The resulting mixture was kept at this temperature for a further 15 min. The solution was then allowed to attain room temperature and stirred for 64 h. It was then filtered through a cannula under nitrogen and the solvent removed under reduced pressure. The product was recrystallised from dilute (10/90) dichloromethane/hexane at -78°C . The mother liquor was syringed off and the product dried under reduced pressure.

3.5. Preparation of $[\text{Cp}(\text{CO})_2(\text{PPh}_i\text{Me}_{3-i})\text{Mo}(\text{CH}_2)_n\text{W}(\text{CO})_3\text{Cp}]$ $i = 0$ to 3, $n = 3, 4$

Solutions of the salts $\text{Na}[\text{Cp}(\text{CO})_2(\text{PPh}_i\text{Me}_{3-i})\text{Mo}]$ $i = 0$ to 3 (0.484 mmol) in THF (25 ml), were prepared

by reducing the respective dimers, $[\text{Cp}(\text{CO})_2(\text{PPh}_i\text{Me}_{3-i})\text{Mo}]_2$ (0.242 mmol) with a Na (0.25 g, 10.87 mmol)/Hg (6 ml) amalgam. The solution was then added dropwise over 30 min to a stirred solution of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{I}\}]$ (0.484 mmol, $n = 3, 4$) in THF (5 ml) maintained at -78°C . The resulting solution was stirred for a further 15 min at this temperature, and then allowed to attain room temperature before stirring for a further 3 days. The solvent was removed under reduced pressure, leaving a greenish/yellow residue, which was extracted with dichloromethane (3×10 ml) and filtered via a cannula under nitrogen. The filtrate was reduced, under reduced pressure, to approximately a third of the total volume of the dichloromethane used. The yellow product was precipitated with hexane, and the mother liquor syringed off. The product was washed three times with hexane and dried under reduced pressure. Elemental Anal.: Found (Calc.): **6b** C 38.45 (38.63) H 3.89 (3.97)%.

3.6. Preparation of $[\text{Cp}(\text{CO})_2(\text{PPh}_i\text{Me}_{3-i})\text{Mo}(\text{CH}_2)_n\text{Fe}(\text{CO})_2\text{Cp}]$ $i = 0$ to 3, $n = 3, 4$

The dimers $[\text{Cp}(\text{CO})_2\text{Mo}(\text{PPh}_i\text{Me}_{3-i})]_2$ $i = 0$ to 3 (0.28 mmol) were reduced to their respective anions $[\text{Cp}(\text{CO})_2\text{Mo}(\text{PPh}_i\text{Me}_{3-i})]^-$ $i = 0$ to 3 (0.56 mmol) by Na (10.87 mmol)/Hg (6 ml) in THF (25 ml). The solution of the anion was added dropwise over 30 min to a stirred solution of $[\text{Cp}(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{I}\}]$ $n = 3, 4$ (0.555 mmol) dissolved in THF (5 ml) at -78°C . The solution was stirred for 15 min at this temperature, then allowed to attain room temperature and stirred for a further 5 days. The solvent was removed under reduced pressure leaving a yellow/black residue, which was extracted with dichloromethane (3×10 ml) and filtered via a cannula under nitrogen. The filtrate was concentrated under reduced pressure to approximately a third of the total volume of dichloromethane used originally. This solution was transferred to a short alumina column made up with hexane and the product was eluted with 90% dichloromethane/hexane. The resulting solution was concentrated and cooled to -78°C under nitrogen for 30 min. The yellow product separated from the solution. The mother liquor was syringed off and the product dried under reduced pressure.

An alternative workup involved adding degassed alumina (~ 5 g) to the filtrate after the extraction with dichloromethane. The solution was again filtered through a cannula into another Schlenk tube. This solution was then reduced to a third of the total volume and the product precipitated with hexane. This method gave better yield and cleaner products. Elemental Anal.: Found (Calc.): **7b** C 60.02 (60.02), H 4.96 (4.49); **9b** C 52.77 (52.92), H 5.08 (4.95); **10b** C 47.90 (47.93), H 5.23 (5.17)%.

3.7. Crystallography

3.7.1. Growth of crystals

Slightly more than one equivalent volume of hexane was added to a concentrated solution of compound **3a** or **7a** in dichloromethane, in a vial. This mixture was left to stand in a refrigerator at $-10\text{ }^{\circ}\text{C}$. The crystals grew by slow solvent diffusion after several days [47].

3.7.2. Data collection

X-ray data for compounds **3a** and **7a** were collected on a CAD-4 diffractometer. In both cases the unit cell was determined from 25 reflections ($\theta = 12^{\circ}$) and found to be consistent with a monoclinic lattice for which a complete set of data was collected by the ω - 2θ scan method for $\theta = 2^{\circ}$ to 23° . The data were reduced with application of Lorentz and polarization correction factors with the program XCAD (Oscail V8) [48]. Correction for absorption was applied using the program DIFABS (Oscail V8) [49]. Further details are given in Table 5.

3.7.3. Structure solution and refinement

Both structures were solved in the monoclinic space group $P2_1/c$ by direct methods using, for **3a** the program DIRDIF [50], as implemented by the crystallographic program WinGX [51], and for **7a** SHELXS-97 [52], as implemented by the crystallographic program Oscail [49]. In both cases E-maps led to the location of all non-hydrogen atoms which were then refined anisotropically with the program SHELXL-97 [52]. In the final stages of refinement all hydrogen atoms were included as idealized contributors in the least-squares process with standard SHELXL-97 idealization parameters. There was no evidence (difference Fourier map) for the inclusion of solvent in the lattice in either case. Further details of the refinement process are available in Table 5. Structural drawings were prepared using the program ORTEP [51]. PLATON was used for the geometry calculations providing bond lengths and angles in terms of the centroids of the Cp rings [53].

3.7.4. Analysis of complexes **2a**, **5b** and **10a** by liquid chromatography time-of-flight mass spectrometer

The samples were analysed by direct infusion liquid chromatography (LC) coupled with the LECO Jaguar® Time-of-Flight Mass Spectrometer (TOF-MS). Approximately 1.7 mg of each complex was dissolved in 2 ml acetonitrile. Of the 2 ml solution, 1 ml was diluted to 10 ml with acetonitrile and injected into the instrument with a flow rate of $1.5\text{ }\mu\text{l}/\text{min}$.

4. Supplementary material

Cif format X-ray structural data are deposited with the Cambridge Crystallographic Data Centre, CCDC

nos. 203294 for $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$ (**3a**) and 203295 for $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$ (**7a**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Tel.+44 1223 336408; Fax +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk, linstead@ccdc.cam.ac.uk, or <http://www.ccdc.cam.ac.uk>). Full tables of atomic positional parameters, thermal parameters, interatomic distances and angles, and torsional angles for **3a** and **7a** are available from the authors.

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