

Reaction studies on some functionalized alkyl transition metal compounds and the crystal structure of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{NO}_2\}]$

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Abstract

The reactions of the halogenoalkyl compounds $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{X}\}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $n = 3\text{--}5$; $\text{X} = \text{Br}, \text{I}$) and $[\text{Cp}(\text{CO})_2(\text{PPhMe}_2)\text{Mo}\{(\text{CH}_2)_3\text{Br}\}]$ with the nucleophiles $\text{Z} = \text{CN}^-$ and N_3^- gave compounds of the type $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{Z}\}]$ for the tungsten compounds, whilst cyclic carbene compounds were obtained from the reactions of the molybdenum compound. The reactions of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{Br}\}]$ ($n = 3, 4$) and $[\text{Cp}(\text{CO})_2(\text{PPhMe}_2)\text{Mo}\{(\text{CH}_2)_3\text{Br}\}]$ with NO_3^- gave $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{ONO}_2\}]$ and $[\text{Cp}(\text{CO})_2(\text{PPhMe}_2)\text{Mo}\{(\text{CH}_2)_3\text{ONO}_2\}]$, respectively. The reaction of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{Br}\}]$ with AgNO_2 gave $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{NO}_2\}]$. In the solid state the complex $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{NO}_2\}]$ crystallizes in a distorted square pyramidal geometry. In this molecule the nitropropyl chain deviates from the ideal, all-*trans* geometry as a result of short, non-hydrogen intermolecular $\text{N}\cdots\text{O}\cdots\text{N}$ contacts. The reactions of the heterobimetallic compounds $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\}\text{ML}_y]$ ($\{\text{ML}_y = \text{Mo}(\text{CO})_3\text{Cp}, \text{Mo}(\text{CO})_3\text{Cp}^*$ and $\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}$; $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5\}$ with PPh_3 and CO were found to be totally metalselective, with the ligand always attacking the metal site predicted by the reactions of the corresponding monometallic analogues above with nucleophiles. Thus the compounds $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\}\text{C}(\text{O})\text{ML}_z]$ ($\{\text{ML}_z = \text{Mo}(\text{CO})_2\text{YCp}, \text{Mo}(\text{CO})_2\text{YCp}^*$ and $\text{Mo}(\text{CO})\text{Y}(\text{PMe}_3)\text{Cp}$; $\text{Y} = \text{PPh}_3$ or CO) were obtained. Similarly, the reaction of $[\text{Cp}(\text{CO})_2\text{Fe}\{(\text{CH}_2)_3\}\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ with CO gave only $[\text{Cp}(\text{CO})_2\text{Fe}\{(\text{CH}_2)_3\}\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$. Hydrolysis of the bimetallic compound, $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})(\text{PPh}_3)(\text{PMe}_3)\text{Cp}]$, gave the carboxypropyl compound $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{COOH}\}]$. Thermolysis of the compound $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Mo}(\text{CO})_3(\text{PMe}_3)\text{Cp}]$ gave cyclopropane and propene, indicating that β -elimination and reductive processes had taken place.

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1. Introduction

When compared to halogenomethyl transition metal compounds, longer-chain halogenoalkyl compounds have been comparatively little studied [1]. Indeed, only those of platinum [2], ruthenium [3], iron [4], tungsten [5,6] and recently molybdenum [6] have been studied in any detail. The application of some of these compounds in organic synthesis has been described [1], but few reaction studies on these compounds have been reported. Importantly, compounds of the type $[\text{L}_y\text{M}\{(\text{CH}_2)_n\text{X}\}]$ (L_yM = transition

metal and its associated ligands, $n \geq 1$, X = halogen) are known precursors of cyclic carbene complexes [1] as well as homo- and heterodinuclear alkanediyl compounds [1,7,8]. Heterobimetallic alkanediyl compounds are proposed to be good precursors or models for catalytic intermediates. It is believed that their study may lead to improved understanding of processes such as the Fischer–Tropsch, olefin polymerization, catalytic oxidation, hydrogenation and hydroformylation reactions, as well as of CO activation [9,10]. With the growing global supply of linear paraffins and the limited supply of traditional industrial feedstocks, the study of the activation of alkanes is also gaining importance [11]. Information on the nature of the chemical activities of heterodinuclear metal functionalized

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paraffins is therefore of interest. Few of these complexes are known and therefore few reaction studies have been carried out on them.

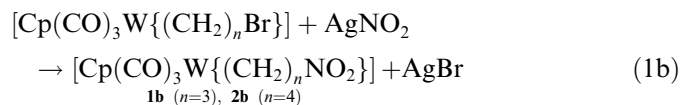
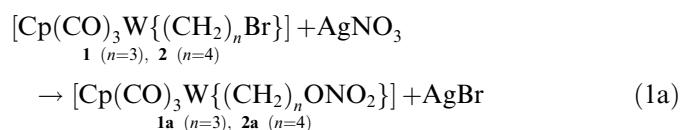
We have previously reported the synthesis of the haloalkyl compounds $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{X}\}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $n = 3\text{--}6$; $\text{X} = \text{Br}, \text{I}$) and $[\text{Cp}(\text{CO})_2(\text{PPhMe}_2)\text{Mo}\{(\text{CH}_2)_n\text{X}\}]$ ($n = 3, 4$) [6], and the heterobimetallic alkanediyl compounds $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{ML}_y\}]$ ($\text{ML}_y = \text{Mo}(\text{CO})_3\text{Cp}, \text{Mo}(\text{CO})_3\text{Cp}^*$ ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$), $\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}$) [8] and $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Ru}(\text{CO})_2\text{Cp}]$ [12], and now report on reaction studies carried out on some of these compounds.

2. Results and discussion

2.1. Reactions of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{X}\}]$ ($n = 3\text{--}5$; $\text{X} = \text{Br}, \text{I}$)

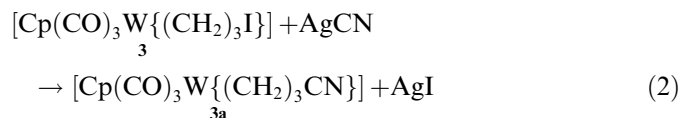
The compound $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{Br}\}]$ (**1**) was reacted with silver nitrate in acetonitrile at room temperature to give an orange product. Significant effervescence was noted on the addition of the AgNO_3 and the analytical data obtained for the product implied a mixture of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{ONO}_2\}]$ (**1a**) and $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{NO}_2\}]$ (**1b**). Repeating the reaction at 0°C in the dark with $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{Br}\}]$ (**2**) gave $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{ONO}_2\}]$ (**2a**) only (Eq. (1a)). Apart from the elemental analysis data, the key diagnostic feature was intense IR peaks at 1622 and 1280 cm^{-1} , assignable to the symmetric and asymmetric $\text{N}=\text{O}$ stretching of a covalent nitrate, respectively [13]. The reaction of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{Br}\}]$ with AgNO_2 at 0°C in the dark gave the yellow nitrobutyl compound $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{NO}_2\}]$ (**2b**) (Eq. (1b)), according to the elemental analysis data and the absence of a peak in its IR spectrum in the region indicative of an organo-nitrate compound [14]. Both **2a** and **2b** are relatively stable and were fully characterized. In contrast, the reaction of **1** at 0°C in the dark with AgNO_3 and AgNO_2 , respectively, gave products which were significantly less stable. Thus compound **1a** is pyrophoric in the solid state with even traces of oxygen, whilst **1b** is unstable in solution at room temperature. The difference in the physical properties of

functionalized propyl transition metal compounds, when compared to longer alkyl chain compounds, has been postulated to be due to an interaction between the metal and the functional group at the end of the propyl chain [4,6]



The ^1H NMR spectra of **2a** and **2b** showed a significant downfield shift of ca. 1 ppm due to the CH_2NO_2 and CH_2ONO_2 protons versus the CH_2Br protons of the starting material [8]. In the ^{13}C NMR spectra the carbon attached to these protons was very deshielded, and found at 72.9 and 75.0 ppm, respectively, compared to 8.16 ppm for the starting material [8], reflecting the strong electronegativity of the nitro and nitrate groups.

Neither **1**, $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{I}\}]$ (**3**), nor $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{I}\}]$ (**4**) reacted with sodium cyanide or potassium cyanide in acetonitrile. However, the reaction of silver cyanide with compound **3** in acetonitrile gave the compound $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{CN}\}]$ (**3a**) (Eq. (2))



A sharp peak at 2244 cm^{-1} , characteristic of $\nu(\text{CN})$ was observed in the infrared spectrum [13]. The ^1H NMR spectrum showed peaks around 3.10 ppm (CH_2CN) and 1.7 pm ($\text{CH}_2\text{CH}_2\text{CN}$) in the upfield region (Table 1). The reaction proceeded slowly, as found by monitoring by ^1H NMR spectroscopy over several days (for the disappearance of the CH_2I peak) and did not reach completion. The ^{13}C NMR spectrum showed a peak at 119 ppm, which is attributable to the cyano group [13].

A change of reaction medium had a significant effect on the reaction. Hence, the reaction of AgCN with **3** in an equi-volume mixture of nitrogen saturated water and tetra-

Table 1
IR, yields and ^1H NMR data from the reaction studies of some of the tungsten haloalkyl compounds

Compound	IR $\nu(\text{CO})^a$ (cm^{-1})	Yield (%)	Cp^b	$\alpha\text{-CH}_2$	CH_2L	$\text{CH}_2\text{CH}_2\text{L}$	$\beta\text{-CH}_2$	$\gamma\text{-CH}_2$
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{CN}\}]$	2012sb, 1914sb	95	5.38s	1.44m	3.10t, 7.2 ^c	1.70m		
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{CN}\}]$	2011sb, 1912sb	92	5.38s	1.46m	3.42t, 7.2	1.84m	1.64m	
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{NO}_2\}]$	2011sb, 1912sb	97	5.36s	1.49m	4.43t, 6.6	1.71m		
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{NO}_2\}]$	2011ss, 1912sb	97	5.38s	1.46m	4.38t, 7.1	1.99m	1.62m	
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{ONO}_2\}]$	2011ss, 1912sb	63	5.38s	1.46m	4.44t, 6.6	1.71m	1.62m	
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{N}_3\}]$	2011ss, 1912sb	98	5.38s	1.45m	3.42t, 6.7	1.85m	1.67m	
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_5\text{N}_3\}]$	2010ss, 1910sb	95	5.35s	1.51m	3.16t, 6.7	1.82m	1.37m	1.47m

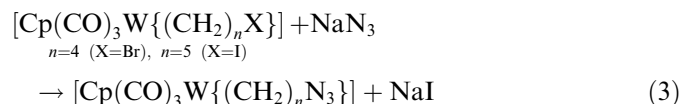
^a Measured in CH_2Cl_2 sb = strong broad, ss = strong sharp.

^b ^1H NMR spectra measured in CDCl_3 relative to TMS ($\delta = 0.00$ ppm), s = singlet, m = multiplet, t = triplet; $\alpha\text{-CH}_2$ refers to the CH_2 -group α to tungsten, etc.

^c J values are given in Hz.

hydrofuran over 4 days gave **3a** in very high yield. Similarly, the reaction of NaCN with **4** in this solvent mixture over 4 days gave the yellow compound $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{CN}\}]$.

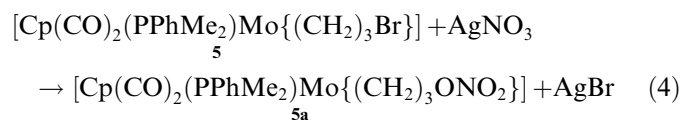
The reactions of the compounds $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{Br}\}]$ and $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_5\text{I}\}]$ with sodium azide gave $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{N}_3\}]$ and $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_5\text{N}_3\}]$, respectively (Eq. (3))



In both of these reactions, there was a change in the $\nu(\text{CO})$ region in the infrared spectrum after only 5 min from the start of the reaction. A medium, broad band was observed at 1639 cm^{-1} , suggesting that an alkyl migration reaction may have occurred. However, no acyl group was seen in the final product. As expected, a weak peak was observed at 2155 cm^{-1} that could be attributed to the stretching vibrations of $-\text{N}=\text{N}^+=\text{N}^-$. Characterization data of the products obtained from the above reactions are listed in Tables 1 and 2.

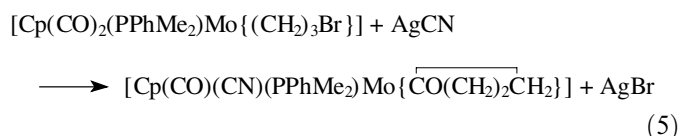
2.2. Reactions of $[\text{Cp}(\text{CO})_2(\text{PPhMe}_2)\text{Mo}\{(\text{CH}_2)_n\text{Br}\}]$ ($n = 3, 4$)

The compound $[\text{Cp}(\text{CO})_2(\text{PPhMe}_2)\text{Mo}(\text{CH}_2)_3\text{Br}]$ (**5**) was reacted with silver nitrate in acetonitrile to form $[\text{Cp}(\text{CO})_2(\text{PPhMe}_2)\text{Mo}\{(\text{CH}_2)_3\text{ONO}_2\}]$ (**5a**) as shown in the following equation:



In the ^1H NMR spectrum, the Cp peak shifted downfield from 4.70 ppm (starting material **5**) to 5.31 ppm (product **5a**), and the triplet at 3.34 ppm (**5**) shifted downfield to 4.33 ppm (**5a**). In the ^{13}C NMR spectrum the Cp signal of the product was observed downfield at 94.93 versus 91.83 ppm (**5**), and the $-\text{CH}_2\text{Br}$ peak moved from 37.69 ppm (**5a**) to 68.14 ppm (**5**).

Compound **5** and silver cyanide were reacted in acetonitrile (Eq. (5)).



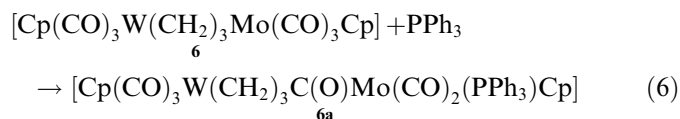
The product was observed to decompose immediately in air. The characterization data obtained for the product suggests that the nucleophile, CN^- , induced cyclization to give a cyclic carbene compound. In particular, a characteristic peak at $\delta = 366$ ppm was observed in the ^{13}C NMR spectrum, which can be assigned to the carbene carbon. Reported alkoxy carbene compounds have carbene carbon peaks in this region [15–17]. Similar results to the above were obtained when the reaction above was repeated in ‘super dry’ ethanol. Whilst cyclic carbene formation is known to occur on the reaction of $[\text{C}_5\text{R}_5(\text{CO})_3\text{Mo}\{(\text{CH}_2)_3\text{Br}\}]$ ($\text{R} = \text{H}, \text{CH}_3$) with CN^- [16], the analogous compound with a bulky PPh_3 ligand, $[\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}\{(\text{CH}_2)_3\text{Br}\}]$, was reported to not react with nucleophiles to give carbene compounds.

The reaction of compound **5** with sodium azide in acetonitrile at room temperature also gave a very unstable cyclic carbene compound, as interpreted from the spectroscopic data obtained. Repeating this reaction at low temperatures (-8 and -40 °C) gave the same product.

2.3. Reactions of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\}\text{ML}_y]$ ($n = 3, \text{ML}_y = \text{Mo}(\text{CO})_3\text{Cp}, \text{Mo}(\text{CO})_3\text{Cp}^*$ and $\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}$ and $n = 4, \text{ML}_y = \text{Mo}(\text{CO})_3\text{Cp}$ and $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$)

2.3.1. Reactions with neutral nucleophiles

The compound $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_3\text{Cp}]$ (**6**) reacted with PPh_3 in acetonitrile to give the orange compound, $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$ (**6a**), as shown in the the following equation:



Monitoring this reaction by infrared spectroscopy showed the growth of an acyl peak at 1712 cm^{-1} and the concurrent disappearance of the band at 1963 cm^{-1} , assigned to a terminal Mo–CO group of the starting material. A sharp

Table 2
 ^{13}C NMR data from the reaction studies of some of the tungsten halogenoalkyl compounds^a

Compound	CO	CN	Cp	$\alpha\text{-CH}_2$	CH_2L	$\text{CH}_2\text{CH}_2\text{L}$	$\beta\text{-CH}_2$	$\gamma\text{-CH}_2$
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{CN}\}]$	228, 217	119.3	91.5	–11.9	11.7	40.9		
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{CN}\}]$	228, 217	119.1	91.0	–12.4	33.5	35.0	38.3	
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{NO}_2\}]$	^b , 217		91.5	–12.3	72.9	32.6		
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{NO}_2\}]$	228, 217		91.5	–13.1	75.0	33.2	33.1	
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{ONO}_2\}]$	228, 217		91.5	–12.3	72.9	32.5	32.6	
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{N}_3\}]$	228, 217		91.0	–12.4	33.6	35.1	38.4	
$[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_5\text{N}_3\}]$	228, 217		91.5	–12.4	33.6	35.1	38.5 ^c	38.5 ^c

^a Measured in CDCl_3 relative to TMS ($\delta = 0.00$ ppm); $\alpha\text{-CH}_2$ refers to the CH_2 -group and α refers to tungsten, etc.

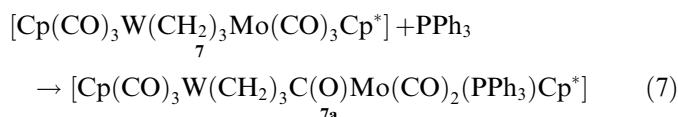
^b Not observed.

^c Peaks overlap.

triplet observed at 3.05 ppm in the ^1H NMR spectrum could be assigned to CH_2 next to an acyl group. Also, the CpMo peak moved upfield from 5.27 (**6**) to 4.97 ppm (**6a**), whilst the position of the Cp peak assigned to tungsten was unchanged, relative to the starting material. In the ^{13}C NMR spectrum, the CpMo peak moved downfield from 92.6 ppm in the starting material to 96.5 ppm. The chemical shift of the WCH_2 peak changed from -5.1 (**6**) to -9.9 ppm (**6a**), the peak in the starting material assigned to MoCH_2 at 7.6 ppm had disappeared and was replaced by a peak due to MoC(O)CH_2 at 71.1 ppm, while the MoCH_2CH_2 peak moved from 44.3 (**6**) to 33.2 ppm (**6a**). The ^{13}C NMR chemical shift for the acyl carbon was observed downfield at 267 ppm. Similar compounds had acyl carbon peaks around 261 ppm [7]. The data thus clearly show that a migratory insertion reaction [18] had taken place exclusively at the molybdenum end of the molecule. Compound **6**, when reacted with two equivalents of PPh_3 in the same solvent, also gave **6a** only i.e. no reaction at the tungsten end of the molecule occurred.

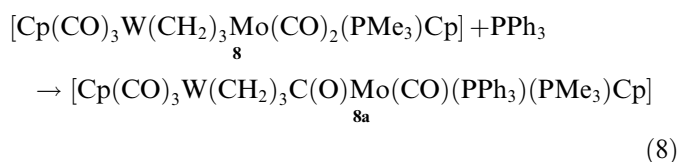
Compound **6** and PPh_3 were refluxed in tetrahydrofuran (THF) for 5 days. An acyl band was observed in the IR spectrum after two days at 1710 cm^{-1} . The IR and the ^1H and ^{13}C NMR spectra of the final product showed the presence of PPh_3 but not of the acyl group, implying that a decarbonylation reaction had followed the alkyl migration reaction, giving the compound $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$ (**6b**).

The complex, $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_3\text{Cp}^*]$ (**7**), when reacted with PPh_3 in CH_3CN also underwent a migratory insertion reaction to yield an unstable complex, $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C(O)Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}^*]$ (**7a**), as shown in the following equation:



A strong band due to an acyl carbonyl group was observed at 1704 cm^{-1} in the IR spectrum. The product showed a triplet downfield at 2.33 ppm due to $\text{CH}_2\text{C(O)}$ in the ^1H NMR spectrum. This downfield shift relative to compound **6a** was expected because Cp^* is a better electron donor than Cp, increasing the electron density on the molybdenum centre, which in turn causes a downfield shift of the signal due to protons adjacent to the acyl group. The reactions of compound **7** with excess PPh_3 in CH_3CN or with PPh_3 in refluxing THF also gave only compound **7a**.

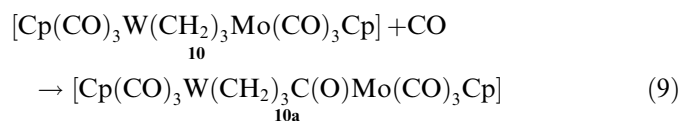
The compound $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**8**) also reacted with equimolar or excess quantities of PPh_3 , resulting in the formation of the acyl compound **8a** shown in the following equation:



A peak due to an acyl group in the infrared spectrum at 1603 cm^{-1} and a triplet observed at ca. 2.9 ppm in the ^1H NMR spectrum due to $\text{CH}_2\text{C(O)}$ confirmed that a migratory insertion reaction had taken place. Peaks due to both of the phosphine substituents were present in the NMR spectra. The chemical shift of the carbon α to molybdenum was shifted downfield, from 10.47 (**8**) to 31.85 ppm (**8a**, now adjacent to the acyl group) in the ^{13}C NMR spectrum, confirming the site of attack. The molybdenum side of the molecule was thus still more reactive than the tungsten side and a metalloselective reaction with PPh_3 had occurred, despite the presence of the basic trimethylphosphine substituent on the Mo, which should lower the reactivity towards nucleophiles. Trimethylphosphine also has a larger Tolman cone angle (118°) than the CO ligand (95°) [19], but clearly provided little steric hindrance to further substitutions taking place on the molybdenum site. The reaction of compound **8** with the more basic PMe_3 gave the less stable compound, $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C(O)Mo}(\text{CO})(\text{PMe}_3)_2\text{Cp}]$ (**8b**), which decomposed on melting at room temperature.

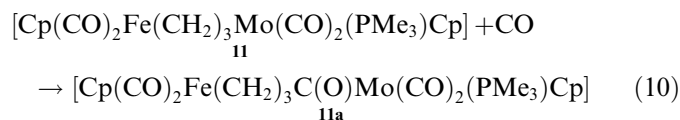
The hydrolysis of compound **8a** at 5°C in a hexane/dichloromethane solution gave yellow crystals of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_2\text{COOH}\}]$ (**9**), which were characterized by X-ray crystallography [20]. Compound **8a** may form the carboxylic acid derivative by attack of a hydroxyl group, from water, on the acyl group and displacing the $\text{Mo}(\text{CO})(\text{PMe}_3)(\text{PPh}_3)\text{Cp}$ moiety as shown in Scheme 1.

Bubbling carbon monoxide gas through a solution of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_3\text{Cp}]$ (**10**) in acetonitrile yielded the unstable acyl complex, $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C(O)Mo}(\text{CO})_3\text{Cp}]$ (**10a**), as shown in the following equation:

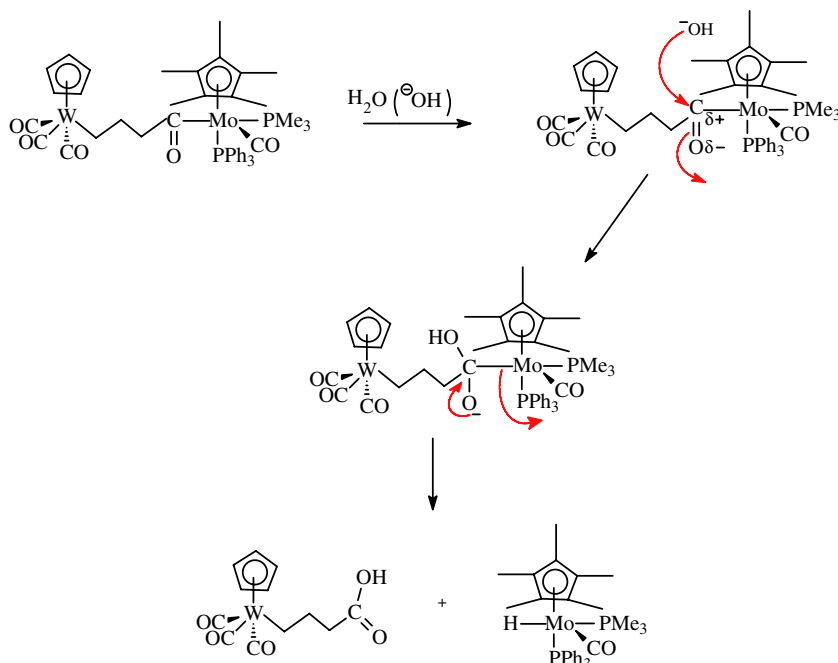


An acyl peak was observed in the infrared spectrum of **10a** at 1604 cm^{-1} , as was a triplet due to the protons next to the acyl group at around 3.72 ppm in the ^1H NMR spectrum. Again the reaction took place selectively at the molybdenum center, since the chemical shift of the CpMo was observed at 5.36 ppm in the ^1H NMR spectrum of **10a** compared to the CpMo shift at 4.88 ppm in **10** [8]. The CpW peak shifted only slightly from 4.71 (**10**) [8] to 4.97 ppm (**10a**). This compound was too unstable for a ^{13}C NMR spectrum to be recorded.

The complex $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**11**) also reacted with carbon monoxide gas in acetonitrile to yield $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{C(O)Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**11a**) (Eq. (10)).



A strong peak at 1603 cm^{-1} due to the acyl group was observed in the carbonyl region of the infrared spectrum.

Scheme 1. Possible pathway to the compound $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{COOH}\}]$.

The high basicity of the substituent PMe_3 seems to stabilize the CO-inserted product by increasing the electron density on the metal. Consequently, a ^{13}C NMR spectrum could be obtained. The ^1H NMR spectrum showed a triplet at 2.90 ppm corresponding to the CH_2 protons adjacent to the carbonyl group. The ^{13}C NMR spectrum showed a shift of ca. 5 ppm observed for the CpMo (from 90.85 ppm in **11** [8] to 95.06 ppm), $\text{MoC}(\text{O})\text{CH}_2$ 70.86 ppm, FeCH_2 3.87 ppm (versus 9.60 in **11**) and the central carbon of the alkyl chain at 33.88 ppm compared to 46.10 ppm [8]. The CpFe peak of the product shifted only slightly (by

0.16 ppm) relative to the starting material, and this further supports the conclusion that Mo was the site of attack. This chemistry thus parallels the reaction of $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Mo}(\text{CO})_3\text{Cp}]$ with CO, where only the Mo centre is attacked [7]. Thus the greater basicity and bulk of the PMe_3 versus CO coordinated to the molybdenum again does not hinder attack, as was also observed for the reaction of **8** with PPh_3 as described above.

Characterization data for the above compounds are given in Tables 3–5 and a summary of the reactions is shown in Scheme 2.

Table 3

Yields, melting point and IR data from the reaction studies on some of the heterobimetallic compounds

Compound	Yield (%)	MP ($^\circ\text{C}$)	IR $\nu(\text{CO})$ (cm^{-1}) ^a			
$[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})(\text{PMe}_3)(\text{PPh}_3)\text{Cp}]$	88	78–84	2010s	1912sb	1843sh	1603w
$[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_4\text{C}(\text{O})\text{Mo}(\text{CO})(\text{PMe}_3)_2\text{Cp}]$	92	dec.	2010s	1911sb	1838sh	1604w
$[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$	90	118–124	2002s	1940sb	1843vsb	1793wb
$[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_3\text{Cp}]$	98	dec.	2010s	1979vsb	1911vsb	1604wb
$[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}^*]$	93	82–86	2011ss	1912sb	1844sm	1704s
$[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$	89	146–148	2009ss	1911sb	1850ss	1613wb
$[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$	98	dec	1998s	1938vs	1921s	1713ss

^a Measured in CH_2Cl_2 , s = strong, sb = strong broad, ss = strong sharp, vs = very strong, vsb = very strong broad, w = weak, wb = weak broad.

Table 4

^1H NMR data from the reaction studies on some of the heterobimetallic compounds^a

Compound	CpMo	Cp*Mo	CpW/Fe	β -Mo	α -W/Fe	γ -Mo	δ -Mo	P-Ph	P-CH ₃
$[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})(\text{PMe}_3)(\text{PPh}_3)\text{Cp}]$	5.27s		5.39s	2.93t, 7.5 ^b	0.86s	2.35s		7.36m	1.52d, 9H, 9.3
$[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_4\text{C}(\text{O})\text{Mo}(\text{CO})(\text{PMe}_3)_2\text{Cp}]$	5.10s		5.35s	2.93t, 7.3	0.85s	2.33s	1.60m		1.54d, 18H, 12.8
$[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}^*]$		2.00	5.39s	2.33t, 7.2	1.64s	2.13s		7.53m	
$[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$	5.36s		4.97s	3.05t, 6.9	1.43s	1.65m		7.44m	
$[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$	5.10s		4.70s	2.95t, 7.4	1.34s	1.61s			1.57d, 9H, 9.6

^a Measured in CDCl_3 relative to TMS (0.00 ppm), α -CH₂ refers to the CH₂-group α to molybdenum, etc.

^b J values in Hz.

Table 5
 ^{13}C NMR data from the reaction studies on some of the heterobimetallic compounds^a

Compound	MoCO	MoC=O	W/Fe CO	CpMo	Cp*(C)	Cp*(CH ₃)	CpW/Fe	β-Mo	α-W/Fe	γ-Mo	δ-Mo	Ph	P-Me
[Cp(CO) ₃ W(CH ₂) ₃ C(O)Mo(CO)(PMe ₃)(PPh ₃)Cp]	237d, 24.4 ^b	176	217	95.0			91.5	39.3	-12.1	31.9		128	18.4
[Cp(CO) ₃ W(CH ₂) ₄ C(O)Mo(CO)(PMe ₃) ₂ Cp]	228d, 24.1	176	^c	94.0			91.5	36.4	-11.5	33.0	30.6		18.4
[Cp(CO) ₃ W(CH ₂) ₃ C(O)Mo(CO) ₂ (PPh ₃)Cp*]	^c	^c	217		104	10.93	91.5	39.6	-12.0	31.9		128	
[Cp(CO) ₃ W(CH ₂) ₃ C(O)Mo(CO) ₂ (PPh ₃)Cp]	238d, 22.6	267	217	96.5			91.5	71.1	-9.9	33.2		128	
[Cp(CO) ₂ Fe(CH ₂) ₃ C(O)Mo(CO) ₂ (PMe ₃)Cp]	237d, 24.1	^c	217	95.1			85.3	70.9	3.8	33.9			21.0

^a Measured in CDCl₃ relative to TMS (0.00 ppm); β-Mo refers to the carbon atom of the alkyl chain β to Mo, etc. All peaks, unless otherwise indicated, are singlets.

^b J values in Hz.

^c Not observed.

2.3.2. Thermal decomposition

The thermal decomposition of [Cp(CO)₂Fe(CH₂)₃Mo(CO)₂(PMe₃)Cp] (**11**) was investigated. The condensed gaseous products were identified by ¹H NMR spectroscopy. A singlet due to cyclopropane was observed at 0.2 ppm along with peaks at 5.6 ppm (–CH=CH₂), 3.7 ppm (–CH=CH₂), 1.8 ppm (–CH₃) which were assigned to propene, an expected product from this type of reaction. The dimers [Cp(CO)₂Fe]₂ and [Cp(CO)₂(PMe₃)Mo]₂ were shown to be the main components of the dark red solid residue (IR, ¹H NMR [6]).

The mechanism for this type of reaction has been reported to follow a β-elimination and reductive process as shown for the proposed thermolysis of **11** in Scheme 3. We obtained propene and cyclopropane in the ratio of approximately 4:1 for the thermolysis of **11** versus a ratio of approximately 1:1.3 reported for [Cp(CO)₂Fe(CH₂)₃Ru(CO)₂Cp] [21], reflecting the influence of the different metals.

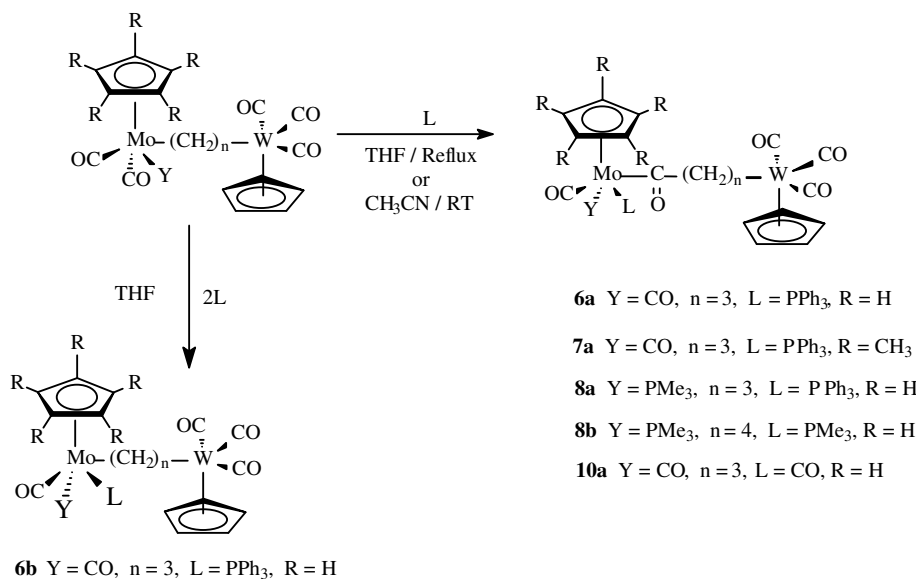
2.4. Crystal structure of [Cp(CO)₃W(CH₂CH₂CH₂NO₂)]

The structure of [Cp(CO)₃W(CH₂CH₂CH₂NO₂)] (**1b**) is, to our knowledge, the first report of a crystal structure of a nitropropyl transition metal complex. Three related functionalized propyl structures of the general formula Cp(CO)₃W(CH₂CH₂CH₂Z) have been reported, with Z = Br (**1**) [6], Z = I (**3**) [22] and Z = COOH (**9**) [20].

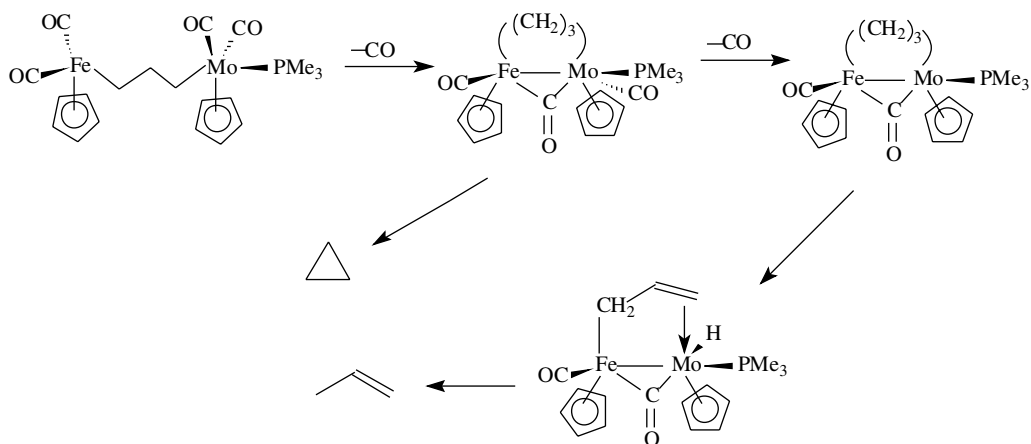
The asymmetric unit is comprised of one molecule, with four molecules in the unit cell. Fig. 1 illustrates the molecular geometry and atomic numbering scheme employed. In the molecule, the W atom is coordinated in a piano stool fashion by a pentahapto-cyclopentadienyl ligand, three carbonyl ligands and a nitropropyl chain bonded through a carbon atom. This geometry can also be viewed as distorted square pyramidal, where a single bond to the centroid of the cyclopentadienyl ligand at the apex of the square pyramid is assumed. Related compounds **1**, **3** and **9** also adopt this coordination geometry in the solid state.

The C atoms constituting the cyclopentadienyl ring are co-planar, with an r.m.s. deviation of 0.002 Å, and the C_{Cp}–C_{Cp} bond lengths range from 1.411(6) to 1.420(5) Å. The five W–C bond lengths vary from 2.304(4) to 2.379(4) Å, and fall within the normal range. A W–C9 bond length of 2.330(4) Å is observed, a value that compares well with W–C_{alkyl} bond lengths reported for related structures (2.347(15) and 2.336(14) Å for **1**, 2.329(5) Å for **3** and 2.319(4) Å for **9**).

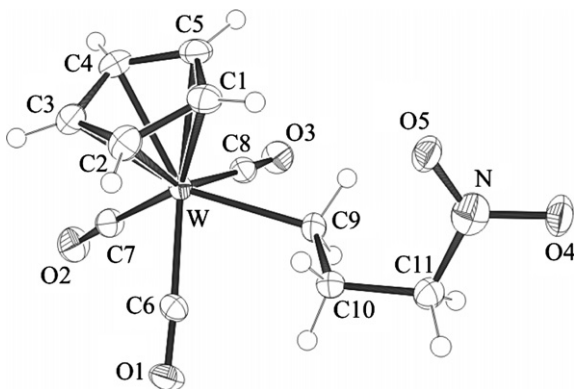
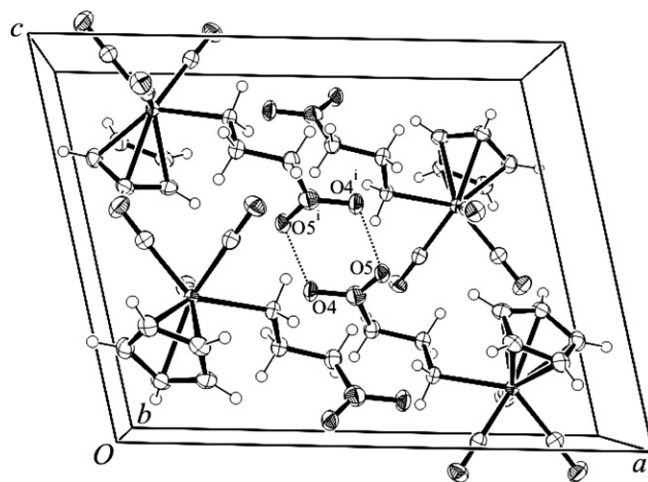
The nitropropyl chain is distorted from the ideal, energetically favoured, all-*trans* conformation (indicated by a torsion angle of 180°), with a C9–C10–C11–N torsion angle of 77.4(4)°. This distortion occurs to allow N–O···O–N close contact interactions between the oxygen atoms on pairs of neighbouring nitro groups. These short, non-hydrogen intermolecular contacts involve atoms O4 and O5 (symmetry operator: 1 – x, – y, – z) and O5 and O4 (symmetry operator: 1 – x, – y, – z), which approach each other at an O···O distance of 2.624 Å, and results



Scheme 2. Summary of the reactions of heterobimetallic complexes.



Scheme 3. Proposed thermolysis pathway for compound 11.

Fig. 1. Molecular diagram of **1b**, illustrating the atomic numbering scheme and displacement ellipsoids at the 50% probability level.Fig. 2. Packing diagram of **1b**, viewed down the *b*-axis. The short contacts between atoms O4 and O5^{*i*}, and O4^{*i*} and O5 (symmetry code for *i*: 1 - *x*, - *y*, - *z*) are illustrated by the dashed lines.

in the formation of a centrosymmetrical dimer, illustrated in Fig. 2. It is interesting to note that this deviation from ideal geometry is also observed for **9**, where an O–H...O carboxylic acid dimer hydrogen bonding interaction is present. However, in structures **1** and **3** the halogenopropyl chains adopt an extended, all-*trans* conformation.

The molecular packing, as viewed down the *b*-axis, is illustrated in Fig. 2. A layered structure is formed in which a two-dimensional sheet containing the interdigitated nitropropyl moieties alternates with a bilayer sheet of CpW(CO)₃ groups. These layers extend parallel to the *bc*-plane of the unit cell. The plane through the C atoms of the cyclopentadienyl carbon is tilted by 61.88(13)° relative to the layer plane.

3. Conclusions

The reaction studies carried out on the halogenoalkyl compounds have shown that the terminal carbon is always attacked in the tungsten complexes to give direct substitution products. The reactions of the molybdenum compounds are more complex, with a nitroalkyl compound forming on reaction with AgNO₃, but other nucleophiles (CN⁻, N₃⁻) attack the molybdenum to induce the formation of cyclic carbene compounds. The molybdenum centre is thus significantly more reactive towards nucleophiles than is the tungsten centre.

Investigations into the chemistry of the alkanediyl compounds, where the iron or tungsten and molybdenum centres were incorporated within the same molecule, showed metalselective reactions. The reaction sites, and hence sites of possible alkyl functionalization, were predictable from the chemistry of the monometallic analogues with nucleophiles and the molybdenum centre was thus found to be very reactive, even in those cases where a tertiary phosphine ligand was already present.

4. Experimental

All reactions were carried out under inert atmosphere using standard Schlenk tube techniques. Acetonitrile (Merck 99%) was distilled over phosphorus pentoxide (Associated Chemical Enterprises 99%) and stored over molecular sieves 4 Å under nitrogen. Methanol (Crest Technical grade) and ethanol (NCP 99.9%) were distilled over CaCl₂ or Mg/I₂ to obtain a 'super dry' solvent according to the reported method [23]. Dichloromethane (Shalom technical grade) and chloroform (Spectrochem 99.5%) were double distilled and kept under molecular sieves 3 Å under nitrogen. All other details are as previously reported [8].

4.1. Crystallography

Good quality single crystals of Cp(CO)₃W(CH₂CH₂-CH₂NO₂) (**1b**) were obtained by crystallization from a dilute CH₂Cl₂/hexane solution in a refrigerator at 5 °C. A yellow, plate-like crystal of dimensions 0.05 × 0.20 × 0.20 mm was selected for the crystallographic investigation. Intensity

data were collected on an Oxford Excalibur2 CCD area detector diffractometer, employing ω -2 θ scans, with Mo K α radiation ($\lambda = 0.71073$ Å) at 150 K. Data collection and cell refinement were performed with the program CRY-SALIS CCD 170 [24], and data reduction was carried out using the program CRY-SALIS RED 170 [24]. In total, 9233 reflections were measured, of which 3200 were independent and $2789 > 2\sigma(I)$, $R_{\text{int}} = 0.0402$ and $\theta_{\text{max}} = 29.40^\circ$. Absorption corrections were performed employing the Multiscan [25] programme. The crystal structure was solved by SHELXS-97 [26] and refined by least squares methods (refinement on F^2) using SHELXL-97 [26] as part of the WinGX [27] suite of programs. All hydrogen atoms were placed in calculated positions and refined using a riding model. A geometric analysis of the molecule was performed with the program PLATON [28] in the WinGX [27] suite. Molecular diagrams were generated with the computer programme ORTEP3 [29]. Compound **1b** crystallizes in the monoclinic space-group $P2_1/c$, with unit cell parameters $a = 14.228(8)$ Å, $b = 8.054(6)$ Å, $c = 11.120(7)$ Å and $\beta = 103.23(5)^\circ$. The final refinement gave values of $R[F^2 > 2\sigma(F^2)] = 0.0243$ and $wR(F^2) = 0.0647$ for 163 parameters. Table 6 lists selected bond lengths, bond angles and torsion angles.

4.2. [Cp(CO)₃W{(CH₂)₄NO₂}]

A solution of [Cp(CO)₃W{(CH₂)₄Br}] (**2**) (0.43 g, 0.84 mmol) in acetonitrile (10 ml) was prepared and cooled to 0 °C and silver nitrite (0.17 g, 0.108 mmol) added in the

Table 6
Selected bond lengths (Å), angles (°) and torsion angles (°)

<i>Bond lengths (Å)</i>	
C9–C10	1.526(5)
C10–C11	1.531(5)
C11–N	1.520(5)
N–O5	1.218(5)
N–O4	1.321(4)
W–C6	1.992(4)
W–C7	1.993(4)
W–C8	1.967(4)
W–C9	2.330(4)
C6–O1	1.141(4)
C7–O2	1.147(5)
C8–O3	1.150(5)
<i>Bond angles (°)</i>	
O5–N–C11	123.3(4)
O5–N–O4	123.5(4)
O4–N–C11	113.2(3)
C10–C9–W	117.4(3)
N–C11–C10	113.7(3)
C9–C10–C11	112.0(3)
O3–C8–W	177.1(3)
O2–C7–W	177.4(4)
O1–C6–W	177.4(3)
<i>Torsion angles (°)</i>	
C11–C10–C9–W	–168.3(2)
C9–C10–C11–N	77.4(4)
C10–C11–N–O5	11.2(5)
C10–C11–N–O4	–170.0(3)

dark. The mixture was stirred at 0 °C overnight. The reaction was monitored in the $\nu(\text{CO})$ region of the infrared spectrum. The solvent was then removed under reduced pressure leaving a mixture of yellow and grey solids. This was extracted with a 4:1 mixture of hexane and dichloromethane and filtered through a cannula under nitrogen. The solvent was removed at reduced pressure to give a yellow solid (**2b**) which was dried under reduced pressure. The IR spectrum showed the expected typical $\nu(\text{N}=\text{O})$ stretches at 1553 cm^{-1} (asym) and 1382 cm^{-1} (sym). Found (Calc.): C, 33.8 (33.1); H, 3.0 (3.0); N, 2.6 (3.2)%.

4.3. $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{ONO}_2\}]$

A solution of $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{Br}\}]$ (**2**) (0.47 g, 0.91 mmol) in acetonitrile (6 ml) was prepared and cooled to 0 °C and silver nitrate (0.169 g, 1.00 mmol) added in the dark. The mixture was stirred at 0 °C overnight. The reaction was monitored in the $\nu(\text{CO})$ region of the infrared spectrum. The solution was filtered via cannula under nitrogen into a pre-weighed Schlenk tube. The solvent was then removed under reduced pressure leaving a pale yellow solid (**2a**). This was washed with hexane and dried under reduced pressure. The IR spectrum showed the expected typical $\nu(\text{N}=\text{O})$ stretches at 1622 cm^{-1} (asym) and 1280 cm^{-1} (sym) and 869 cm^{-1} . Found (Calc.): C, 32.4 (32.0); H, 3.1 (2.9); N, 2.8 (3.1)%.

4.4. $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{Z}\}]$ ($\text{Z} = \text{NO}_3$ and NO_2)

These compounds (**1a** and **1b**) were prepared as in Sections 4.2 and 4.3.

4.5. $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_n\text{CN}\}]$ ($n = 3, 4$)

The compound $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_3\text{I}\}]$ (**3**) (0.106 g, 0.21 mmol) was weighed into a Schlenk tube. Silver cyanide (0.03 g, 0.22 mmol) was added, followed by a mixture of nitrogen saturated double distilled de-ionized water (2 ml) and THF (2 ml). The mixture was stirred for 4 days. The solvent was removed under reduced pressure and the product recrystallized from a dichloromethane/hexane mixture and dried under reduced pressure.

A similar reaction was carried out using **4** and NaCN instead of AgCN, and $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{CN}\}]$ was obtained.

4.6. $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{N}_3\}]$

The compound $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_4\text{Br}\}]$ (**2**) (0.1 g, 0.22 mmol) and sodium azide (0.015 g, 0.213 mmol) were weighed into an empty Schlenk tube. The Schlenk tube was evacuated and then filled with nitrogen and acetonitrile (7 ml) was subsequently added. There was a notable change in the $\nu(\text{CO})$ region in the IR spectrum after 5 min. At the end of the reaction, as determined by no further changes in the IR spectrum, the solution was filtered via cannula under nitrogen into a pre-weighed Schlenk tube. The solvent was

removed under reduced pressure leaving a yellow solid, which was washed with hexane and dried under reduced pressure.

4.7. $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_5\text{N}_3\}]$

This was prepared by a procedure similar to that described in Section 4.6 using $[\text{Cp}(\text{CO})_3\text{W}\{(\text{CH}_2)_5\text{I}\}]$ (0.054 g, 0.103 mmol).

4.8. $[\text{Cp}(\text{CO})_2(\text{PPhMe}_2)\text{Mo}\{(\text{CH}_2)_3\text{ONO}_2\}]$

The compound $[\text{Cp}(\text{CO})_2(\text{PPhMe}_2)\text{Mo}\{(\text{CH}_2)_3\text{Br}\}]$ (**5**) (0.130 g, 0.257 mmol) and AgNO_3 (0.04 g, 0.257 mmol) were dissolved in acetonitrile (5 ml) and stirred for 24 h. The resulting yellow solution was filtered through a cannula, under nitrogen into a pre-weighed Schlenk tube. The solvent was removed under reduced pressure and the product (**5a**) recrystallized from a dilute dichloromethane/hexane mixture. The orange precipitate was collected and dried under reduced pressure. Yield = 95%; IR $\nu(\text{CO})$ (CH_2Cl_2): 1922 (sb), 1910 (ss); $^1\text{H NMR}(\text{CDCl}_3)$ in ppm: 5.31 (singlet, Cp), 1.77 (multiplet, Mo- CH_2), 1.99 (multiplet, Mo- CH_2CH_2), 4.33 (triplet, CH_2ONO_2), 7.42 (multiplet, P-Ph), 1.70 (doublet, P- CH_3 , $J_{\text{PH}} = 10.2$ Hz); $^{13}\text{C NMR}(\text{CDCl}_3)$: 94.9 (Cp), 14.0 (Mo- CH_2), 38.7 (Mo- CH_2CH_2), 68.1 (CH_2ONO_2), 128 (doublet, P-Ph, $J_{\text{PC}} = 9.7$ Hz), 18.4 (doublet, P- CH_3 , $J_{\text{PC}} = 32.8$ Hz).

4.9. $[\text{Cp}(\text{CO})(\text{N}_3)(\text{PPhMe}_2)\text{Mo}\{\overline{\text{CO}(\text{CH}_2)_2\text{CH}_2}\}]$

Compound **5** (0.08 g, 0.174 mmol) and NaN_3 (0.011 g, 0.175 mmol) were weighed into a Schlenk tube, dissolved in acetonitrile (8 ml) and stirred for 24 h. The solution was then filtered via cannula under nitrogen and the solvent removed under reduced pressure. The residue was recrystallized from a dilute dichloromethane/hexane mixture to give an orange precipitate. Yield = 90%. IR $\nu(\text{CO})$ (CH_2Cl_2): 1967 (sb), 1911 (ss); $^1\text{H NMR}(\text{CDCl}_3)$ in ppm: 5.30 (singlet, Cp), 3.59 (multiplet, Mo= CCH_2), 1.97 (multiplet, Mo= CCH_2CH_2), 4.71 (multiplet, OCH_2), 7.44 (multiplet, P-Ph), 1.74 (doublet, P- CH_3 , $J_{\text{HH}} = 8.4$ Hz); $^{13}\text{C NMR}(\text{CDCl}_3)$: 94.5 (Cp), 62.1 (Mo= CCH_2), 22.0 (Mo= CCH_2CH_2), 84.8 (OCH_2), 128 (doublet, P-Ph, $J_{\text{PC}} = 9.7$ Hz), 19.4 (doublet, P- CH_3 , $J_{\text{PC}} = 34$ Hz).

4.10. $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$

(a) The complex $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_3\text{Cp}]$ (**6**) (0.11 g, 0.178 mmol) and PPh_3 (0.047 g, 0.179 mmol) were weighed into a Schlenk tube and dissolved in acetonitrile (4 ml). The resulting solution was stirred at room temperature for 3 days and monitored by IR spectroscopy in the $\nu(\text{CO})$ region. The solution was concentrated under reduced pressure and the product, a yellow precipitate, was filtered off. To recrystallize, the product was dissolved in minimum dry dichloromethane and an equal volume of hexane

was added. The mixture was immersed in a cold dry-ice–acetone bath ($-60\text{ }^{\circ}\text{C}$) for a minute. The mother liquor was decanted and the residue dried under reduced pressure to give **6a** as a yellow powder.

- (b) The reaction above was repeated with 1:2 molar ratio of the compounds i.e. compound **6** (0.11 g, 0.178 mmol) and PPh_3 (0.094 g, 0.358 mmol) in acetonitrile (4 ml). All further details were as above.
- (c) A mixture of **6** (0.105 g, 0.17 mmol) and PPh_3 (0.044 g, 0.17 mmol) was weighed into a Schlenk tube and dissolved in a minimum of THF (8 ml). The resulting solution was refluxed, while monitoring the changes in the carbonyl region of the infrared spectrum twice a day. No further changes were observed on days 8 and 9. The reaction was allowed to cool to room temperature under nitrogen. The solvent was then removed under reduced pressure. A red residue was obtained which was dissolved in a minimum of dichloromethane and the yellow product precipitated using hexane. The product (**6a**) was filtered off and dried under reduced pressure.

4.11. $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$

The above reaction was repeated with a 2:1 ratio of PPh_3 (0.084 g, 0.320 mmol) and **6** (0.10 g, 0.161 mmol) in THF (8 ml). Again the changes were monitored using IR in the carbonyl region of the IR spectrum, and the reaction was judged to be complete after 5 days. Work-up of the product was repeated as above and a yellow product (**6b**) was obtained which was dried and characterized. Yield = 84%. The IR $\nu(\text{CO})$ (CH_2Cl_2) in cm^{-1} : 2010 ss, 1913 sm, 1870 ss, 1848 sh; m.p.: $182\text{--}185\text{ }^{\circ}\text{C}$; ^1H NMR (CDCl_3) in ppm: 7.4 (multiplet, Ph), 5.38 (singlet, WCp), 4.74 (singlet, MoCp), 1.97, 1.65, 0.86 ($\text{CH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (CDCl_3) in ppm: 128.49 (doublet, Ph, $J_{\text{PC}} = 12.3\text{ Hz}$), 91.53, 95.83 (Cp), -11.06 (W– CH_2), 1.01 (Mo– CH_2), 31.57 (W– CH_2CH_2).

4.12. $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cp}^*]$

- (a) The compound $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_3\text{Cp}^*]$ (**7**) (0.20 g, 0.29 mmol) and PPh_3 (0.076 g, 0.29 mmol) were weighed into a Schlenk tube and the mixture dissolved in acetonitrile (4 ml). The solution was stirred at room temperature for 3 days, after which the solvent was removed under reduced pressure. The yellow product was dissolved in minimum dry dichloromethane. Dry hexane was added until the product just started to precipitate. The mixture was then immersed in a dry-ice–acetone bath ($-60\text{ }^{\circ}\text{C}$) for 2 min. The mother liquor was decanted and the residue dried under reduced pressure to give **7a** as a yellow powder.
- (b) The above reaction (a) was repeated in a 1:2 molar ratio. The compound **7** (0.20 g, 0.29 mmol) was reacted with PPh_3 (0.152 g, 0.58 mmol) in acetonitrile (4 ml) at room temperature for 4 days. Work-up was as reported in (a) above.

4.13. $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})(\text{PMe}_3)(\text{PPh}_3)\text{Cp}]$

- (a) The complex $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**8**) (0.098 g, 0.173 mmol) was dissolved in acetonitrile (5 ml) and PPh_3 (0.038 g, 0.146 mmol) was added. The mixture was stirred at room temperature until no more changes were observed in the $\nu(\text{CO})$ region in the IR spectrum (18 h). An orange precipitate had also formed. The solvent was removed under reduced pressure. The residue was dissolved in minimum dichloromethane and the product **8a** precipitated with hexane to give a light yellow solid.
- (b) The above reaction was repeated in a 1:2 molar ratio of **8** to PPh_3 to give the same compound (**8a**) as in (a) above in 72% yield.

4.14. $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_4\text{C}(\text{O})\text{Mo}(\text{CO})(\text{PMe}_3)_2\text{Cp}]$

A solution of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_4\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**8**) (0.10 g, 0.172 mmol) and PMe_3 (0.013 g, 0.172 mmol) was made up in acetonitrile (5 ml). The mixture was stirred at room temperature for 3 days while monitoring the reaction progress using ^1H NMR spectroscopy. The orange solution was evaporated to dryness under reduced pressure to leave a light yellow residue, which was dissolved in minimum of dichloromethane, filtered and the product (**8b**) precipitated with hexane.

4.15. $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_3\text{Cp}]$

The complex $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_2)_3\text{Mo}(\text{CO})_3\text{Cp}]$ (**10**) (0.186 mmol) was dissolved in acetonitrile (5 ml) in a Schlenk tube and sealed with a rubber suba seal. Using a slender, flexible Teflon tube, carbon monoxide gas was bubbled into the solution. The reaction was followed by observing changes in the $\nu(\text{CO})$ region in the infrared spectrum. A strong, sharp acyl band was observed in the carbonyl region of the IR spectrum. The bubbling was stopped after 30 h. The product was dried under reduced pressure and recrystallized from a dichloromethane/hexane mixture. The product (**10a**) obtained was unstable and was only partially characterized.

4.16. $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{C}(\text{O})\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$

Reaction conditions were as above, except that $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**11**) (0.15 g, 0.31 mmol) was dissolved in acetonitrile (5 ml) to give **11a** after reaction and work-up.

4.17. Thermal decomposition of $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$

The compound $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**11**) (0.1 g, 0.21 mmol) was weighed into a Schlenk tube, which was connected to a second Schlenk tube containing CDCl_3 immersed in liquid nitrogen. The system was evac-

uated. The Schlenk tube containing **11** was heated to decomposition. The gaseous products were trapped in the Schlenk tube immersed in the liquid nitrogen. The solid residue after the heating was red in colour. The condensed gaseous products dissolved into the CDCl_3 when the solution was allowed to attain room temperature. The ^1H NMR spectrum of the solution was obtained. The data obtained were as follows: (propene) 5.60, 3.73, 1.83 ppm and (cyclopropane) 0.223 ppm.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 279095. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.07.003](https://doi.org/10.1016/j.jorganchem.2006.07.003).

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