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Reactions of $\mu(\alpha,\omega)$-alkanediyl complexes of iron(II) and tungsten(II) with tertiary phosphines and halogens; a mechanistic study

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Abstract

Reactions of the $\mu(\alpha,\omega)$alkanediyl complexes $[(Cp)(CO)_2Fe(CH_2)_nFe(CO)_2(Cp)]$ with neutral donor ligands initially give the monosubstituted monoacyl complexes $[(Cp)L(CO)FeC(O)(CH_2)_nFe(CO)_2(Cp)]$, which then react further to give the disubstituted diacyl complexes $[(Cp)L(CO)FeC(O)(CH_2)_nC(O)Fe(CO)L(Cp)]$ (where $Cp = \eta^5\text{-}C_5H_5$; $n = 3\text{–}7$ and $L = PPh_3$, PPh_2Me or PMe_3). Similar reactions of $[(Cp)(CO)_3W(CH_2)_nW(CO)_3(Cp)]$ with the ligands L give the disubstituted diacyl complexes $[(Cp)L(CO)_2WC(O)(CH_2)_nC(O)W(CO)_2L(Cp)]$, although these latter reactions are considerably slower. In contrast to the reactions of the diiron compounds, the reactions of the dinuclear di-tungsten compounds also give the mono- and di-substituted alkanediyl compounds $[(Cp)L(CO)_2W(CH_2)_nW(CO)_3(Cp)]$ and $[(Cp)L(CO)_2W(CH_2)_nW(CO)_2L(Cp)]$. The reactions of the alkanediyl compounds of iron with halogens causes cleavage of both iron–carbon bonds and yield $[CpFe(CO)_2X]$ and $X(CH_2)_nX$. The mechanisms of these reactions are discussed.

Introduction

There is considerable current interest in transition metal complexes in which a hydrocarbon group bridges two or more metal atoms [1]. This is in part because such complexes can be models for catalytic intermediates but also because new fundamental processes may be identified for binuclear or polynuclear complexes that are not possible for mononuclear metal complexes.

One group of compounds in this class are the $\mu(\alpha,\omega)$-alkanediyl complexes $LM(CH_2)_nML$ (where ML is metal and associated ligands).

Such compounds can be models for a C_nH_{2n} fragment interacting with two active sites on a catalyst surface. Although a large number of such compounds have now been prepared [2–4] their reactions have not been studied in detail. For the di-iron compounds $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ (n = 3 or 4) it has been shown that they will

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undergo migratory insertion reactions with CO [5] to give diacyl species, and for the compounds in which $n = 3$ reaction with SO_2 gives the mono- and di-sulphinato insertion products [6].

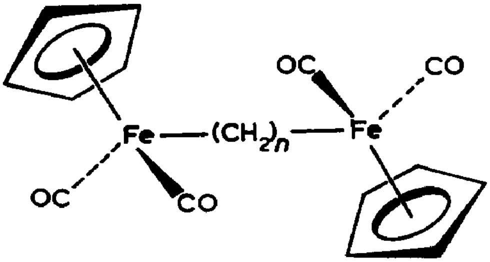
We now report on our results of the reactivity of two series of alkanediyl compounds, namely $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ ($n = 3$–7) and $[CpW(CO)_3]_2[\mu\text{-}(CH_2)_n]$ ($n = 3$–5) with tertiary phosphine ligands and with halogens. We were particularly interested to see whether these compounds would show any differences in reactivity from that of their mononuclear alkyl analogues, and also to see whether we could observe differences in reactivity that are dependent on the length of the polymethylene chain in the alkanediyl complexes.

Results and discussion

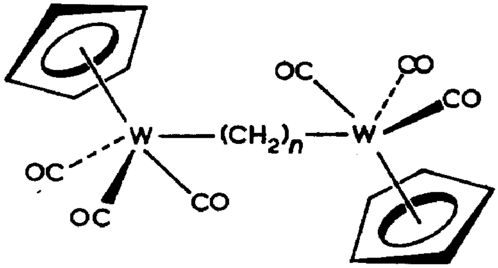
Reactions of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ with the tertiary phosphines PPh_3, PPh_2Me or PMe_3

The mononuclear alkyliron compounds of the type $[CpFe(CO)_2R]$ react with tertiary phosphines on heating to yield phosphine-substituted acyl compounds [7]. Similarly, we find that the reactions of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ with tertiary phosphines also undergo thermal reactions to yield acyl products. However, the reactions of the binuclear alkanediyl compounds give different products depending on the nature of the ligand and the amount of ligand used. Thus, either the monosubstituted monoacyl compounds (**3**) or the disubstituted diacyl compounds (**4**) may be isolated as the major products. For example, $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_3]$ (**1a**) on reaction with PPh_3 (1/1 mole ratio) gives $[(Cp)(PPh_3)(CO)FeC(O)(CH_2)_3Fe(CO)_2(Cp)]$ (**3a**) in 64% yield (eq. 1) whereas the reaction of **1a** with PPh_3 (1/2 mole ratio) gives the disubstituted diacyl species **4a** as the major product (eq. 2).

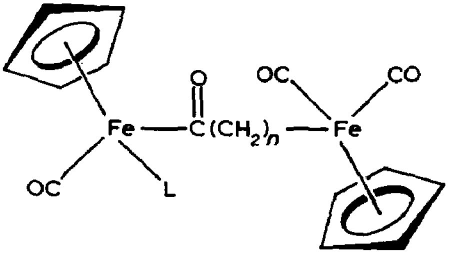
$$\underset{\textbf{(1a)}}{[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_3]} + PPh_3 \rightarrow \underset{\textbf{(3a)}}{[(Cp)(PPh_3)(CO)FeC(O)(CH_2)_3Fe(CO)_2(Cp)]} \quad (1)$$



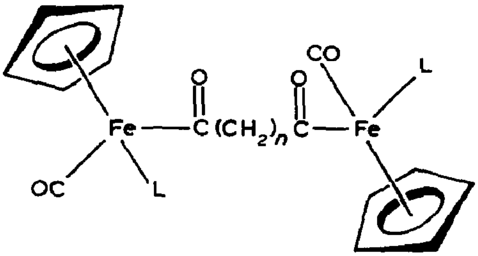
(**1a** $n = 3$;
1b $n = 4$;
1c $n = 5$;
1d $n = 6$;
1e $n = 7$)



(**2a** $n = 3$;
2b $n = 4$;
2c $n = 5$)



(**3a** $n = 3$ L = PPh_3)



(**4a** $n = 3$ L = PPh_3 ;
4b $n = 4$ L = PPh_3 ;
4c $n = 5$ L = PPh_3 ;
4d $n = 6$ L = PPh_3 ;
4e $n = 7$ L = PPh_3 ;
4f $n = 3$ L = $PMePh_2$;
4g $n = 4$ L = $PMePh_2$;
4h $n = 3$ L = PMe_3)

$$\underset{\textbf{(1a)}}{[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_3]} + 2PPh_3 \rightarrow$$

$$\underset{\textbf{(4a)}}{[(Cp)(PPh_3)(CO)FeC(O)(CH_2)_3C(O)Fe(CO)(PPh_3)(Cp)]} \quad (2)$$

Similarly, the reactions of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ ($n = 4$–7; **1b**–**1e**) with PPh_3 (1/2 mole) in refluxing THF for 36–48 hours gave the disubstituted diacyl compounds **4b**–**4e**, respectively; traces of the monosubstituted monoacyl compounds **3** were also detected. The reaction of **1a** with $PMePh_2$ (1/3.5 mole) in THF under reflux gave **4f** in good yield after 18 h. Under the same conditions, **1b** reacted with $PMePh_2$ to give an analogous complex **4g** in 86% yield after only 6 h (i.e. the reaction is much faster for the $(CH_2)_4$ than for the $(CH_2)_3$-bridged compound). The reaction of **1a** with a large excess of PMe_3 gave **4h** in 79% yield after 42 h in THF under reflux.

The compounds **3a** and **4a**–**4h** were all isolated as orange microcrystalline solids and characterized by IR and ^1H NMR spectroscopy and microanalysis (see Tables 1–3 and Experimental Section). The compounds **3** and **4** are stable in air in the solid state but solutions, particularly in hydrocarbon solvents, decompose on exposure to air to non-carbonyl decomposition products. The IR spectra of the diacyl species **4a**–**4h** resemble those of mononuclear compounds of the type $[CpFe(CO)(PPh_3)\text{-}COR]$ [8], which show a single terminal $\nu(CO)$ band in the region 1906 to 1913 cm^{-1}, this position reflects the π-acceptor properties of the phosphine ligand. A broad band at 1600 cm^{-1} for the acyl groups was also observed. The monoacyl compound **3a** shows three terminal carbonyl bands of approximately equal intensity which correspond in position, as might be expected, to those of **1a** and **4a**.

The ^1H NMR spectrum of **3a** shows, as expected, two singlet Cp proton resonances and an approximate triplet for the CH_2CO protons in the ratio 5/5/2. The signal for the remaining methylene protons is an unresolved doublet. In the ^1H NMR spectra of the diacyl species **4a**–**4h** the methylene proton resonances are more complex. All the spectra show a complex multiplet for the four CH_2CO protons and two broad singlets for the other methylene protons. In a variable temperature ^1H

Table 1

Reaction times, products and yields for the compounds $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ (n = 3–7) with tertiary phosphine (L) in mole ratio (1/2)

Compound	L	Reaction time (h)	Products (yield)	
1a	PPh_3	66	$[Cp(CO)(PPh_3)Fe\{CO(CH_2)_3\}Fe(CO)_2Cp]$ (**3a**)	(12%)
			$[Cp(CO)(PPh_3)Fe\{CO(CH_2)_3CO\}Fe(CO)(PPh_3)Cp]$ (**4a**)	(57%)
1b	PPh_3	48	$[Cp(CO)(PPh_3)Fe\{CO(CH_2)_4CO\}Fe(CO)(PPh_3)Cp]$ (**4b**)	(69%)
1c	PPh_3	48	$[Cp(CO)(PPh_3)Fe\{CO(CH_2)_5CO\}Fe(CO)(PPh_3)Cp]$ (**4c**)	(68%)
1d	PPh_3	42	$[Cp(CO)(PPh_3)Fe\{CO(CH_2)_6CO\}Fe(CO)(PPh_3)Cp]$ (**4d**)	(76%)
1e	PPh_3	36	$[Cp(CO)(PPh_3)Fe\{CO(CH_2)_7CO\}Fe(CO)(PPh_3)Cp]$ (**4e**)	(88%)
1a	$PMePh_2$	18	$[Cp(CO)(PMePh_2)Fe\{CO(CH_2)_3CO\}Fe(CO)(PMePh_2)Cp]$ (**4f**)	(62%)
1b	$PMePh_2$	6	$[Cp(CO)(PMePh_2)Fe\{CO(CH_2)_4CO\}Fe(CO)(PMePh_2)Cp]$ (**4g**)	(86%)
1a	PMe_3	42	$[Cp(CO)(PMe_3)Fe\{CO(CH_2)_3CO\}Fe(CO)(PMe_3)Cp]$ (**4h**)	(79%)

NMR study of **4a** and **4d** no change in the methylene proton signals was detected over the range −40 to +80°C. However, below −20°C some splitting of the cyclopentadienyl resonance of **4a** was observed. Furthermore, the extent of the splitting of the methylene proton signals does not vary noticeably with increasing length of the alkanediyl bridge in compounds **4a**–**4e** or with decreasing bulk of the tertiary phosphine substituents (compounds **4a**, **4f**, **4h**) as it might be expected to do if it were due to restricted rotation in the molecule. The splitting of the methylene proton signals could arise from the diastereomeric shielding of these protons by the asymmetric $[CpFe(CO)(L)]$ groups. In this case, the two protons in each CH_2CO group would be non-equivalent and coupling between these protons could give rise

Table 2

Melting points and elemental analyses of $[Cp(CO)(L)Fe\{CO(CH_2)_nCO\}Fe(CO)(L)Cp]$ (n = 3–7; L = tertiary phosphine)

Compound	Melting point (°C)	Analysis (found (calcd.)(%))	
		C	H
4a	105–110	69.0	5.0
		(69.2)	(5.0)
4b	100–104	69.6	5.1
		(69.3)	(5.1)
4c	64–68	69.9	5.4
		(69.6)	(5.3)
4d	85–95	70.0	5.4
		(69.8)	(5.4)
4e	82–86	69.8	5.8
		(70.0)	(5.5)
4f	65–68	64.6	5.3
		(64.8)	(5.3)
4g	135–138	65.4	5.7
		(65.2)	(5.4)
4h	134–136	50.5	6.3
		(50.4)	(6.2)

Table 3

IR and ^1H NMR data for [Cp(CO)(L)Fe{CO(CH$_2$)$_n$CO}Fe(L)(CO)Cp] ($n = 3$–7; L = tertiary phosphine)

Compound	IR ν(CO) cm$^{-1\,a}$	^1H NMR; CH$_2$ ^{d}	Chemical shift, CH$_2$CO ^{e}	δ(ppm) ^{b,c} Cp ^{f}	PMe ^{g}
4a	1913(s), 1604(m)	0.89 (1H) 0.26 (1H)	2.60 (4H)	4.35 (10H)	–
4b	1913(s), 1607(m)	0.88 (2H) 1.26 (2H)	2.58 (4H)	4.36 (10H)	–
4c	1912(s), 1603(m)	0.89 (2H) 1.25 (4H)	2.60 (4H)	4.36 (10H)	–
4d	1913(s), 1599(m)	0.88 (2H) 1.26 (6H)	2.65 (4H)	4.36 (10H)	–
4e	1913(s), 1603(m)	0.93 (2H) 1.25 (8H)	2.68 (4H)	4.38 (10H)	–
4f	1912(s), 1595(m)	0.88 (1H) 1.25 (1H)	2.44 (4H)	4.40 (10H)	1.99 (6H)
4g	1911(s), 1595(m)	0.90 (2H) 1.24 (2H)	2.46 (4H)	4.41 (10H)	2.00 (6H)
4h	1906(s), 1596(m)	1.70 (2H)	2.78 (4H)	4.40 (10H)	1.34 (18H)

[a] In CH$_2$Cl$_2$ solution. [b] In CDCl$_3$ solution. [c] For **4a**–**4g** a multiplet at ca. δ 7.4 is observed for the phenyl protons. [d] All signals broad singlets. [e] All signals complex multiplets. [f] All signals doublets with J ca. 1.8 Hz. [g] All signals doublets with J ca. 9 Hz.

to the observed splitting. Such shielding effects have been reported for the compounds [CpFe(CO)(PPh$_3$)(COC$_2$H$_5$)] [9] and [CpFe(CO)(PPh$_3$)(CH$_2$Ph)] [10], and more recently detailed studies on the preferred conformations of alkyl groups attached to the chiral auxillary Fe(Cp)(CO)(PPh$_3$) in mononuclear compounds have been reported [11,12].

The fact that the mono-acyl species **3a** can be isolated from the equimolar reaction of **1a** with PPh$_3$ suggests that the formation of diacyl compounds may proceed in a stepwise fashion. To investigate this an infrared study was made of the reactions of **1a**–**1e** with a two molar ratio of PPh$_3$. The progress of the reactions was followed by observing the disappearance of the ν(CO) bands at ca. 2000 and 1940 cm^{-1} in the infrared spectrum of the reaction mixture, and the accompanying appearance of product ν(CO) bands at ca. 1920 and 1610 cm^{-1}. Initially a rapid decrease in the bands at 2000 and 1940 cm^{-1} to approximately half their original intensity was observed. After this point, further decrease was slow and the rate was found to depend on the length of the alkanediyl bridge in the substrate. This is illustrated in Fig. 1 by the plots of I_t/I_0 against time where I_0 is the intensity of the band at 2000 cm^{-1} at the start of the reaction and I_t its intensity at time t.

These observations are consistent with the reactions' proceeding by initial rapid conversion of the substrate to the monoacyl species **3**. On completion of this reaction, shown in eq. 3, i.e. at the point at which there is a sudden change in reaction rate (see Fig. 1), the IR spectrum of the reaction mixture corresponds to that of the monoacyl product showing bands at ca. 2000 and 1940 cm^{-1} for the terminal carbonyl groups on the unsubstituted iron residue and bands at ca 1920 and 1810 cm^{-1} for the terminal carbonyl group on the other iron and the acyl group

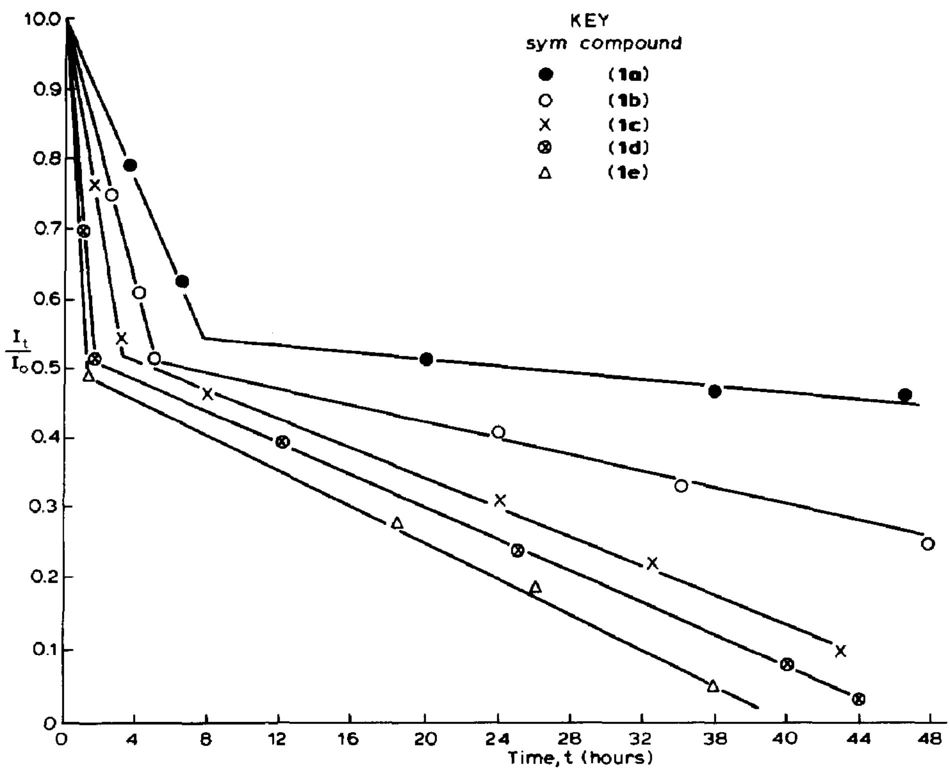


Fig. 1. Plots of I_t/I_0 against time for the reactions of compounds **1a**–**1e** with PPh_3 (where I_0 is the intensity of the ν(CO) band in the IR spectrum at ca. 2000 cm^{-1} at the start of the reaction and I_t is its intensity at time t).

respectively. The monoacyl species then reacts slowly with further PPh_3 to give the diacyl product **4** (eq. 4).

$$\underset{(\mathbf{1})}{[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]} + PPh_3 \rightarrow$$

$$\underset{(\mathbf{3})}{[(Cp)(CO)(PPh_3)FeC(O)(CH_2)_nFe(CO)_2(Cp)]} \qquad (3)$$

$$\underset{(\mathbf{3})}{[(Cp)(CO)(PPh_3)FeC(O)(CH_2)_nFe(CO)_2(Cp)]} + PPh_3 \rightarrow$$

$$\underset{(\mathbf{4})}{[(Cp)(CO)(PPh_3)FeC(O)(CH_2)_nC(O)Fe(CO)(PPh_3)(Cp)]} \qquad (4)$$

The reaction shown in eq. 4 corresponds to the slow decrease in the bands at ca. 2000 and 1940 cm^{-1} due to the monoacyl species. The reaction with a second molecule of PPh_3 may be expected to be slower as a result of the greater steric hindrance to attack by the bulky phosphine group on the monosubstituted acyl species **3**. Thus the dependence of the rate of this reaction on the length of the alkanediyl bridge may reflect a decrease in steric hindrance with increasing distance between the metal atoms.

During the work, several attempts were made to decarbonylate the diacyl compounds **4a**–**4h** to form tertiary phosphine substituted $\mu(\alpha,\omega)$-alkanediyl species. The diacyl compounds **4** are resistant to thermal decarbonylation; for example, **4b** was found to be stable in refluxing dimethoxyethane for prolonged periods. In refluxing petroleum ether (b.p. 130–160 ° C) decomposition of the diacyl compound to a non-carbonyl product was observed.

An established route to compounds of the type [CpFe(CO)(L)R] [8,13] (L = tertiary phosphine; R = alkyl) is via photochemical decarbonylation of the corresponding acyl species [CpFe(CO)(L)(COR)]. However photolysis of $[(Cp)(CO)(PPh_3)FeC(O)(CH_2)_4C(O)Fe(CO)(PPh_3)(Cp)]$ (**4a**) in THF, was found to result in extensive decomposition of the compound and none of the desired product $[CpFe(CO)(PPh_3)]_2[\mu\text{-}(CH_2)_4]$ could be detected. During the photolysis, the infrared spectra of the reaction mixture in the region 2100–1550 cm^{-1} showed the disappearance of starting material bands and the accompanying appearance of bands at 2011, 1991, 1950, 1781, and 1731 cm^{-1}. The bands at 1991, 1950, and 1781 were attributable to $[CpFe(CO_2]_2$ while the band at 2011 cm^{-1} could be due to the presence of a non-substituted acyl species (cf. $[(Cp)(CO)_2FeC(O)(CH_2)_4C(O)Fe(CO)_2(Cp)]$ ν(CO) (THF) 2012(s), 1950(s) cm^{-1}). The appearance of a band at 1732 cm^{-1} suggested that an organic product such as adipic acid could have formed in the reaction. The only organometallic products isolated from the reaction mixture were $[CpFe(CO)_2]_2$ and $[Cp_2Fe]$. It is possible that the photolysis of diacyl compounds might have a synthetic application for the preparation of bifunctional aliphatic compounds from dihaloalkanes. We have also shown that the reaction of $[Mn(CO)_5]_2[\mu\text{-}(CH_2)_4]$ with Br_2 or I_2 in THF yields $HOOC(CH_2)_4COOH$ via initial double CO insertion reactions [14].

The photolysis of **4b** was also carried out in the presence of free PPh_3 to inhibit the dissociation of the tertiary phosphine ligand, and in petroleum ether. Su and Wojcicki [8] have reported good yields of $[CpFe(CO)(PPh_3)R]$ from the photolysis of $[CpFe(CO)(PPh_3)(COR)]$ ($R = CH_3$, C_2H_5) in hydrocarbon solvents. However, in this present study extensive decomposition of $[(Cp)(CO)(PPh_3)FeC(O)(CH_2)_4C(O)Fe(CO)(PPh_3)(Cp)]$ to insoluble non-carbonyl products occurred on photolysis in petroleum ether. Similar results were obtained upon irradiation of $[(Cp)(CO)(PPh_3)FeC(O)(CH_2)_6C(O)Fe(CO)(PPh_3)(Cp)]$ in THF or petroleum ether. $[CpFe(CO)_2]_2$ and an organic product analogous to that observed on photolysis of **4b** were the only isolable products. Thus the binuclear diacyl compounds are more reluctant to undergo decarbonylation than their mononuclear analogues.

An attempt was made to decarbonylate **4b** under milder conditions, namely by reaction with $[RhCl(PPh_3)_3]$ at room temperature, in order to limit sample and product decomposition. However, no reaction was detected after 10 h and the starting diacyl compound **4b** was eventually recovered in 98% yield. The resistance of this compound to chemical decarbonylation can be attributed to the greater strength of the Fe–CO bond in the phosphine-substituted diacyl compound compared with $[(Cp)(CO)_2FeC(O)(CH_2)_nC(O)Fe(CO)_2(Cp)]$ ($n = 3, 4$), which can be decarbonylated.

Alternative routes to phosphine-substituted alkanediyl bridged species were also investigated. Alexander [15] has reported the isolation of $[CpFe(CO)(PPh_3)(CH_3)]$ in 23% yield by irradiation of $[CpFe(CO)_2(COCH_3)]$ in the presence of PPh_3. However, irradiation of a THF solution of $[(Cp)(CO)_2FeC(O)(CH_2)_nC(O)Fe(CO)_2$

(Cp)] ($n = 3, 4$) and an excess of PPh_3 produced mainly $[CpFe(CO)_2]_2$. An organic product similar to that formed in the photolysis of **4b** was detected in these reactions with ν(CO) at 1732 cm^{-1}. A small yield of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$ (19%) was also obtained from the photolysis of $[(Cp)(CO)_2FeC(O)(CH_2)_4C(O)Fe(CO)_2(Cp)]$ in the presence of PPh_3.

Compounds of the type $[CpFe(CO)(PPh_3)R]$ (R = alkyl) have also been prepared by reaction of $[CpFe(CO)_2R]$ with PPh_3 under UV irradiation [8]. On irradiation of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$ in the presence of excess PPh_3 in THF, $[CpFe(CO)_2]_2$ was again formed as the major product. In addition, a band at ca. 1905 cm^{-1} in the infrared spectrum of the reaction mixture suggested the presence of the required product; cf. ν(CO) 1901 cm^{-1} for $[CpFe(CO)(PPh_3)(C_2H_5)]$. After work-up of the reaction mixture, $[CpFe(CO)_2]_2$ and $[(Cp)(CO)(PPh_3)FeC(O)(CH_2)_4C(O)Fe(PPh_3)(CO)(Cp)]$ were isolated in 28 and 16% yield, respectively. Two unstable orange solids were also isolated. One was identified as $[CpFe(CO)(PPh_3)H]$ on the basis of its infrared spectrum and its reaction with $CHCl_3$ to give $[CpFe(CO)(PPh_3)Cl]$. The other showed a strong carbonyl band at 1906 cm^{-1}, which suggested that this was the required product. However, it was unstable and decomposed rapidly in solution and in the solid state to a non-carbonyl product. The compound $[CpFe(CO)(PPh_3)H]$ may have resulted from decomposition of $[CpFe(CO)(PPh_3)]_2[\mu\text{-}(CH_2)_4]$. This type of decomposition has been reported for $[CpFe(CO)(PPh_3)(C_2H_5)]$ [8]. The fact that neither $[CpFe(CO)(PPh_3)]_2[\mu\text{-}(CH_2)_4]$ nor $[CpFe(CO)(PPh_3)H]$ could be detected in the photolysis of **4b** under the same conditions, suggests that **4b** is not formed as an intermediate in reaction (5).

$$[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4] + 2PPh_3 \cancel{\xrightarrow{h\nu}} [CpFe(CO)(PPh_3)]_2[\mu\text{-}(CH_2)_4] \quad (5)$$

Reactions of $\mu(\alpha,\omega)$-alkanediyl diiron compounds with halogens

The reactions of mononuclear iron alkyl compounds $[CpFe(CO)_2R]$ with a wide variety of electrophilic reagents have been studied [16], and there has been much interest in the mechanism of these reactions [17–22]. However, no investigations of the analogous reactions of $\mu(\alpha,\omega)$-alkanediyl diiron compounds have been reported.

In the present work, the reactions of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ ($n = 3, 4$) (**1a** and **1b**) with the halogens I_2 and Br_2 were investigated. Compound **1a** reacted rapidly with both I_2 or Br_2 in 1/2 mole ratio to produce the expected cleavage products as shown in eq. 6.

$$[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_3] + 2X_2 \rightarrow 2[CpFe(CO)_2X] + X(CH_2)_3X \quad (6)$$

$(X = Br, I)$

The products were identified by comparison of their IR and mass spectra with those of authentic samples. In the analogous reaction of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$ with I_2, a third product (ν(CO)(THF): 2080(s), 2046(s) cm^{-1}), in addition to the expected $I(CH_2)_4I$ and $[CpFe(CO)_2I]$, was detected in the infrared spectrum of the reaction mixture, and was isolated as an insoluble, highly unstable red solid **8a**. The insolubility of this compound and the high frequency of the carbonyl bands in its infrared spectrum suggested it was a cationic species (by comparison, the IR spectrum of the cationic species $[CpFe(CO)_2(C_2H_4)]^+$ shows two ν(CO) bands at

2080(s) and 2040(s) cm^{-1}). The cationic nature of **8a** was confirmed by the precipitation of the compound as a yellow tetraphenylborate salt on addition of $NaBPh_4$ to a solution of **8a** in methanol.

The ^1H NMR spectrum of **8a** showed two broad singlets at δ 5.96 and 4.04 ppm; the broadness of these signals may be a consequence of the compound being paramagnetic. Attempts to characterise **8a** further failed, due to its instability particularly under vacuum. Solutions of **8a** in acetone and THF were found to decompose rapidly on standing and the infrared spectra of these solutions showed new ν(CO) bands at 2044, 1999 and 1948 cm^{-1}. The ^1H NMR spectrum of the decomposition products showed the presence of $[CpFe(CO)_2I]$ (δ 5.30, C_5H_5) and $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$ (δ 1.26, CH_2; δ 5.04, C_5H_5).

The reaction of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$ with Br_2 also produced a cationic species: ν(CO) 2076(s), 2044(s); ^1H NMR (acetone-d_6) δ 4.08 (s,8H) 6.0 (s,10H) (**8b**). This compound was isolated as a dark orange solid and was found to be more stable than **8a** in the solid state. As for **8a**, broad proton resonances were observed in the ^1H NMR spectrum of **8b**, consistent with the compounds being paramagnetic. This was confirmed by magnetic susceptibility measurements; a paramagnetic mass susceptibility χ_m of 6.6×10^{-7} m^3 kg^{-1} (5.2×10^{-6} cgsu) was measured for **8b** compared with a value of $\chi_m = -0.5 \times 10^{-6}$ m^3 kg^{-1} for the diamagnetic $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$.

The formation of $[CpFe(CO)_2I]$ and $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$ on decomposition of **8a** suggests that this compound may be an intermediate in the halogen cleavage of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$. Investigations of the kinetics and stereochemistry of reactions of mononuclear alkyliron compounds with various electrophilic reagents [17–22] have indicated that these cleavage reactions may proceed either by a one electron transfer process or via oxidative addition of the electrophile to the substrate molecule.

Both routes involve the formation of a cationic intermediate prior to metal–carbon bond cleavage. Since the cationic species isolated from the reactions of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$ with X_2 are paramagnetic, it appears that the one electron transfer process in eq. 7 may be operative in these reactions. The formulations

$$[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4] + X_2 \rightarrow [(Cp)(CO)_2Fe(CH_2)_4Fe(CO)_2(Cp)]^+[X_2]^- \quad (\mathbf{8a}\text{: } X = I\text{; } \mathbf{8b}\text{: } X = Br) \tag{7}$$

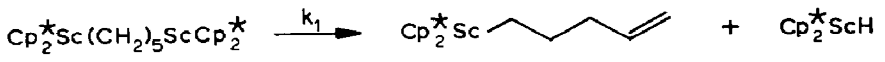
of **8a** and **8b** are consistent with the observed properties of these compounds. The close similarity of their spectral data to that of the cationic species $[CpFe(CO)_2(C_2H_4)]^+$ is suggestive of this structure rather than that of a halide-containing cation. Similarly, the isolation of a yellow BPh_4^- salt of **8a** suggests that the halogen is present only as a counter ion in this species. In addition, decomposition of the BPh_4^- salt of **8a** produces no $[CpFe(CO)_2I]$, only $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$. The final products could be derived from intermediate **8** by attack of X^- leading to $[CpFe(CO)_2\{CH_2)_4X\}]$. Further reaction of $[CpFe(CO)_2\{(CH_2)_4X\}]$ with another molecule of X_2 could result in the formation of the observed $X(CH_2)_4X$. The compound $[CpFe(CO)_2\{(CH_2)_4Br\}]$ [23] was, indeed, found to react with Br_2 to give $[CpFe(CO)_2Br]$ and $Br(CH_2)_4Br$. No intermediate cationic species could be detected in this reaction, but this is not surprising since discrete intermediates have seldom been observed in electrophilic cleavage reactions of mononuclear alkyl iron compounds. The proposal that the cleavage of the metal–carbon bonds in $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ occurs in a stepwise fashion is supported by the observation of small amounts of $[CpFe(CO)_2\{(CH_2)_4X\}]$ (detected by IR and Mass spectroscopy) in the reaction of **1b** with X_2. Cleavage of the Fe–C bond in $[CpFe(CO)_2\{(CH_2)_4X\}]$ apparently occurs more readily than the initial bond cleavage in $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$, since reaction of **1b** with a one molar proportion of X_2 produces $[CpFe(CO)_2X]$ and $X(CH_2)_4X$, and ca. 50% of the starting material **1b** is recovered.

Interestingly and significantly, it has been found that $k_2 > k_1$ in the reactions of the types shown in eq. 8 and 9, where $M = PtMe_2$(1,10-phenanthroline) and $X = I$

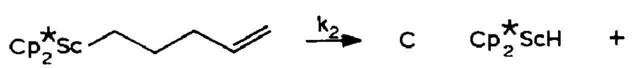
$$M + X(CH_2)_nX \xrightarrow{k_1} XM(CH_2)_nX \tag{8}$$

$$XM\text{-}(CH_2)_nX + M \xrightarrow{k_2} XM(CH_2)_nMX \tag{9}$$

[24] and where M denotes the Rh^I macrocyclic complex and $X = Br$ [25]. Also for the reactions shown in eq. 10 and 11, where $k_1 > k_2$ and $Cp^\star = \eta\text{-}C_5Me_5$) [26].



(10)



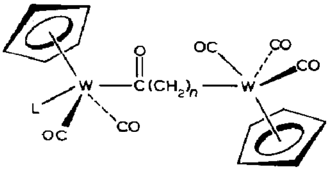
(11)

In the reactions of **1a** with I_2 and Br_2 at 0° C, a cationic species was detected in the IR spectra of the reaction mixtures; This suggests that these reactions proceed by a similar route to those of **1b**, but that the cationic intermediate derived from **1a** is less stable than that from **1b**.

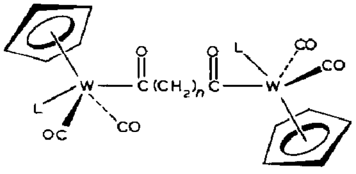
Further studies of these and other $\mu(\alpha,\omega)$-alkanediyl compounds by cyclic voltammetry are under way [27].

Reactions of $\mu(\alpha,\omega)$-alkanediyl ditungsten compounds with tertiary phosphines

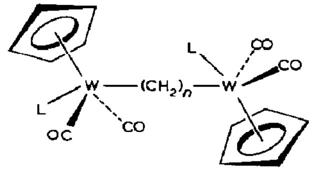
Although there has been considerable interest in the reactions of metal alkyl compounds such as $[CpFe(CO)_2R]$ and $[CpMo(CO)_3R]$ with tertiary phosphines few related reactions of tungsten species have been investigated [13,28]. In the present study, the $\mu(\alpha,\omega)$-alkanediyl ditungsten compounds were found to be considerably less reactive than their diiron analogues. The reactions of **2a**–**2c** with tertiary phosphines generally required high temperatures and/or longer reaction times than those of the corresponding diiron compounds **1a**–**1c**.



(**5a** $n = 5$ $L = PMePh_2$;
5b $n = 4$ $L = PPh_3$)



(**6a** $n = 4$ $L = PMePh_2$;
6b $n = 5$ $L = PMePh_2$;
6c $n = 4$ $L = PPh_3$;
6d $n = 5$ $L = PPh_3$)



(**7a** $n = 4$ $L = PMePh_2$;
7b $n = 5$ $L = PMePh_2$)

Like the diiron compounds, the complexes $[CpW(CO)_3]_2[\mu\text{-}(CH_2)_n]$ react with a two molar proportion of tertiary phosphine to give phosphine-substituted diacyl products. In addition, and in contrast to the reactions of **1a**–**1c** which yield only acyl products **3** and **4**, the reactions of the ditungsten compounds also produce non-acyl substituted compounds in low yield. These species were formulated as $[(Cp)(CO)_2(L)W\{\mu\text{-}(CH_2)_n\}W(CO)_3(Cp)]$ or $[CpW(CO)_2(L)]_2[\mu\text{-}(CH_2)_n]$ (**7**) on the basis of spectroscopic evidence, but could not be separated from the reaction mixtures. The formation of these compounds was indicated by the appearance of a doublet resonance at δ 4.75 in the ^1H NMR spectra of the product mixtures. This could be assigned to the Cp proton resonance of a phosphine substituted alkyl product by comparison with the ^1H NMR spectra of compounds of the type $[CpM(CO)_2(L)(CH_3)]$ [29,30] (L = tertiary phosphine; M = Mo, W).

The reactions of $[CpW(CO)_3]_2[\mu\text{-}(CH_2)_n]$ ($n = 4, 5$) (**2b** and **2c**) with tertiary phosphines in refluxing THF are slow. For example, after 70 h, the diacyl species $[(Cp)(CO)_2(PMePh_2)W\{CO(CH_2)_nCO\}W(PMePh_2)(CO)_2(Cp)]$ ($n = 4., 5$) (**6a** and **6b**) were isolated in only ca. 54% yield from the reactions of **2b** and **2c**, respectively, with $PMePh_2$ (in 1/2 mole ratio) in THF. In refluxing DME, the reaction of **2b** with $PMePh_2$ (in 1/2 mole ratio) gave **6a** in 55% yield after 38 h.

The reaction of **2b** with a two molar proportion of PPh_3 in refluxing DME produced only the monoacyl species $[(Cp)(CO)_2(PPh_3)W\{CO(CH_2)_4\}W(CO)_3(Cp)]$ (**5b**) and a substituted non-acyl product, probably $[(Cp)(CO)_2(PPh_3)W\{(CH_2)_4\}W(CO)_3(Cp)]$, after 34 h. In refluxing THF, a 37% yield of the diacyl species $[(Cp)(CO)_2(PPh_3)W\{CO(CH_2)_4CO\}W(PPh_3)(CO)_2(Cp)]$ (**6c**) was obtained after 75 h. $[CpW(CO)_3]_2[\mu\text{-}(CH_2)_5]$ reacted with PPh_3 (in 1/2 mole ratio) in refluxing THF to give $[(Cp)(CO)_2(PPh_3)W\{CO(CH_2)_5CO\{W(PPh_3)(CO)_2(Cp)]$ (**6d**) in 45% yield after several days.

Compounds **6a**–**6d** were isolated as microcrystalline yellow solids and characterised by IR, ^1H NMR and microanalysis (see Experimental Section). These compounds could exist as *cis*- or *trans*-isomers, but on the basis of their IR and ^1H NMR spectra we have assigned the all *trans* structure (**6**) to them. The IR spectra of these compounds show two terminal $\nu(CO)$ bands (one in the range 1932–1922 and another at 1845 cm^{-1}) with the lower frequency band more intense than the higher frequency band. This intensity pattern has been shown by Manning to be indicative of a *trans* geometry in compounds such as $[CpMo(CO)_2(PPh_3)I]$ [31]. Also, the compounds **6a**–**6d** exhibit a doublet in the ^1H NMR spectra for the cyclopentadienyl resonance due to ^{31}P–^1H coupling (J 1.5 Hz). This splitting is reported to be characteristic of the *trans*-isomer of compounds of the type $[CpM(CO)_2(L)R]$ (L = tertiary phosphine) [10]. In addition, the ^1H NMR spectra of the diacyl species show a well-defined triplet for the CH_2CO protons. If the compounds had contained a *cis*-$[CpW(CO)_2(L)]$ moiety the metal atom would be asymmetric, and diastereomeric shielding of the CH_2CO protons would result in further splitting of this signal [31].

The ^1H NMR spectrum of the monoacyl compound $[(Cp)(CO)_2(PPh_3)W\{CO(CH_2)_4\}W(CO)_3Cp]$ (**5b**) shows a doublet Cp resonance for the $[CpW(CO)_2(PPh_3)]$ moiety indicative of a *trans* geometry about this tungsten atom. In the IR spectrum of **5b** the carbonyl bands from the $[CpW(CO)_2(PPh_3)]$ moieties are superimposed so no information about the geometry of the substituted group can be inferred.

The resistance of $[CpW(CO)_3]_2[\mu\text{-}(CH_2)_n]$ ($n = 3$–5) (**2a**–**2c**) to tertiary phosphine-induced migratory CO-insertion undergone by the analogous diiron compounds, could partly reflect a difference in the metal–alkyl bond strengths. It is generally thought [28,32] that the rate-determining step of a carbonyl insertion reaction, for mononuclear complexes, is the migration of the alkyl group onto a terminal CO to form a coordinatively unsaturated intermediate. If this is so, the slower rate of reaction of the tungsten compounds could be attributed to greater strength of the tungsten–carbon bond of the alkyl groups.

The formation of non-acyl phosphine substituted products in the reaction of $[CpW(CO)_3]_2[\mu\text{-}(CH_2)_n]$ with tertiary phosphine can be attributed to the thermal decarbonylation of acyl products of these reactions (eq. 12 and 13).

$$[(Cp)(CO)_2(L)W\{C(O)(CH_2)_n\}W(CO)_3(Cp)] \rightarrow [(Cp)(CO)_2(L)W(CH_2)_nW(CO)_3(Cp)] \tag{12}$$

$$\begin{aligned}&[(Cp)(CO)_2(L)W\{C(O)(CH_2)_nC(O)\}W(L)(CO)_2(Cp)] \rightarrow\\ &\qquad [(Cp)(CO)_2(L)W\{(CH_2)_nC(O)\}W(L)(CO)_2(Cp)] \rightarrow\\ &\qquad\qquad [CpW(CO)_2(L)]_2[\mu\text{-}(CH_2)_n]\end{aligned} \tag{13}$$

Consistent with this is the observation that the proportion of diacyl product produced in the reaction of **2b** with $PMePh_2$ in DME is decreased, and that of the substituted non-acyl product increased, by prolonged heating of the reaction mixture. In addition, it was found that the diacyl compounds **6a**–**6d** could be converted into non-acyl substituted products by heating than in DME in the presence of an excess of free phosphine ligand. The excess of phosphine is required to inhibit the dissociation of the phosphine ligand; in the absence of free phosphine the diacyl compounds are rapidly converted into the corresponding unsubstituted $\mu(\alpha,\omega)$-alkanediyl compounds **2b** and **2c**. Thus, loss of CO or PR_3 from **6a**–**6d** are competitive processes.

In comparison with compounds of the type $[CpMo(CO)_2(L)COR]$ (L = tertiary phosphine; R = alkyl) [33], the diacyl species **6a**, **6b** and **6d** are relatively resistant to thermal decarbonylation to the corresponding phosphine substituted non-acyl species. Thus, only a trace of a phosphine substituted alkyl product could be detected after heating **6c** in refluxing acetonitrile for 48 h. Among the diacyl tungsten compounds, decarbonylation of the PPh_3 substituted compounds was found to occur more rapidly than that of the $PMePh_2$ substituted species. After 24 h in refluxing DME, ca. 50% conversion of **6d** to a non-acyl product was observed whereas under the same conditions only ca. 10% of **6b** was converted into a non-acyl product (the percentage conversion in these reactions was determined from the relative intensities of the Cp proton resonances of the acyl starting material (ca. δ 5.00 ppm) and the non-acyl product (ca. δ 4.80 ppm) in the ^1H NMR spectra of the reaction mixtures). Similar ligand dependence has been reported for the decarbonylation of $[CpMo(CO)_2(L)(COCH_3)]$ (L = tertiary phosphine) [33], and is thought to be largely steric in origin. The increased rate of decarbonylation with increased size of the tertiary phosphine ligand has been accounted for in terms of a dissociative mechanism in which CO is lost from the substrate to form a coordinatively unsaturated intermediate [CpM(CO)L(COR)]. This dissociation of CO would be favoured by the increased size of L. This mechanism would also be consistent with the electronic effects of L, since the increased basicity of L on going from PPh_3 to

$PMePh_2$ would inhibit dissociation of CO by forcing stronger M–CO back bonding [33].

The stereochemistry of the CO insertion reaction and the reverse decarbonylation is of interest since information can be gained about the reaction mechanisms from their stereochemical results. The exclusive formation of the *trans*-diacyl product in the carbonyl insertion reactions of $[CpW(CO)_3]_2[\mu\text{-}(CH_2)_n]$ is consistent with the reported stereochemistry of the reaction of the mononuclear complexes $[CpM(CO)_3(CH_3]$ (M = Mo, W) with tertiary phosphines to give $[CpM(CO)_2(L)(COCH_3)]$ [33,34]. The formation of the *trans* isomer in these reactions has been attributed to rearrangement of a kinetically favoured *cis* product [13,32]. In the present study, evidence in support of this type of mechanism was provided by the observation of an acyl product with a *cis*-$[CpW(CO)_2(L)]$ configuration in the reaction of **2b** with PPh_3 in THF. This was indicated by the presence of a singlet Cp resonance at δ 5.08 ppm in the ^1H NMR spectrum of the reaction mixture. The detection of the *cis* product suggests that the *cis/trans* isomerisation occurs less readily in the lower boiling solvent. The decarbonylation reactions of $[CpW(CO)_2(L)\{CO(CH_2)_nCO\}W(L)(CO)_2(Cp)]$ (L = PPh_3, $PMePh_2$; $n = 4, 5$) in refluxing DME were found to give only the *trans*-phosphine substituted product. This was indicated by the appearance of a doublet Cp resonance in the ^1H NMR spectra for these compounds. A *trans* product is similarly formed on decarbonylation of $[CpMo(CO)_2(L)(COCH_3)]$ (L = tertiary phosphine), and has been attributed to the preferential migration of the alkyl ligand away from the bulky phosphine group in the unsaturated intermediate [CpM(CO)L(COR)] [33].

Conclusions

In the reactions of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ with PR_3 ligands substitution of CO by PR_3 occurs along with migratory CO insertion. The reaction occurs in a stepwise fashion, with the reaction at the first iron being faster than that at the second iron. The rate of these reactions with PR_3 depends not only on the nature of the PR_3 ligand but also on the number of CH_2 group in the polymethylene chain.

There are differences between these alkanediyl complexes and mononuclear alkyl analogues. Thus, decarbonylation of $[Cp(CO)(L)Fe\{CO(CH_2)_nCO\}Fe(CO)(L)Cp]$ does not occur under conditions in which mononuclear alkyl analogs are decarbonylated. Also, substitution only of CO by PR_3 in $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ is not observed under conditions in which this transformation occurs for $[CpFe(CO)_2R]$ complexes. The intermediate $[CpFe(CO)_2]_2[\mu\text{-}(CH_3)_4]^+$ can be isolated from reactions of the alkanediyl complex with halogens and thus appears more stable than mononuclear counterparts. As with mononuclear alkyl complexes, reactions of these alkanediyl complexes are dependent on the metal and associated ligands, and thus there are different reactivity pathways for the diiron and ditungsten compounds. This study shows that there are differences in the reactivity of these alkanediyl compounds compared to those of their mononuclear analogues. Further studies are underway in our laboratory to obtain more quantitative data on the rates of the reactions observed in these and related systems.

Experimental

All reactions were carried out under high purity nitrogen in dry nitrogen-saturated solvents by Schlenk tube techniques. $[CpW(CO)_3]_2$ was prepared from $[W(CO)_6]$ and [CpNa] by the method described by Manning et al. [35]. The sodium salt of the anion, $Na[CpW(CO)_3]$, was prepared by stirring $[CpW(CO)_3]_2$ with an excess of 5% sodium/mercury amalgam in THF or DME for 1–2 h at room temperature [36]. The diiodoalkanes $I(CH_2)_nI$ ($n = 3$, 4 or 5) were obtained from Fluka A G, Ega-chemie and Riedel de Haen AG, respectively. The compounds $[CpFe(CO)_2]_2]$-μ-$(CH_2)_n]$ ($n = 3$–7) were prepared as previously reported [37]. $[RhX(PPh_3)_3]$ ($X = Cl$, Br) were prepared by the methods described by Wilkinson et al. [38]. The compounds $[CpW(CO)_3]_2[\mu$-$(CH_2)_n]$ ($n = 3$–5) were prepared by known procedures [39,40]. The tertiary phosphines were obtained from Strem Chemicals Inc. and Merck. PMe_3 was produced by Mann and Wells' method [41]. All other reagents were obtained commercially and used without further purification.

Analytical grade solvents were generally used and were purified further when necessary. THF and DME were dried by distillation over $LiAlH_4$ under N_2.

Column chromatography was carried out on BDH silica gel (60–120 mesh) or Merck Aluminium oxide 90 (70–230 mesh). Merck aluminum TLC plates, precoated with silica gel 60, were used for thin layer chromatography.

^1H NMR spectra were recorded on a Varian XL100 spectrometer or on a Bruker WH90 instrument operating in the Fourier Transform mode. Tetramethylsilane was used as internal reference.

IR spectra were recorded on a Perkin–Elmer 983 spectrophotometer in solution using solution cells with NaCl windows and a 0.1 mm path length or as a Nujol mulls on NaCl plates. In the description of IR spectra the following abbreviations are used; (w) = weak, (m) = medium, (s) = strong, (vs) = very strong and (sh) = shoulder.

The low resolution electron impact mass spectra were recorded on a VG micromass 16F spectrometer operating at 70 eV with an accelerating voltage of 4 kV, and the data were analysed on a VG 2000 data system. The unprocessed mass spectrum was also recorded, as a UV trace, on an EMI SE 6150 UV Oscillograph so that metastable peaks and ions with abundances below the detection limit of the data system could be observed. The samples were introduced into the spectrometer as solids on a direct probe at room temperature. Probe and ion source temperatures used for samples **2a**–**2c** was ca. 200 ° C.

Magnetic susceptibilities were determined by the Gouy method on a Gallenkamp magnetobalance. Calibration was with $[Hg(Co(CSN)_4)]$, and the measurements were carried out at room temperature. The samples were finely ground prior to introduction into the Gouy tube. A diamagnetic correction of -5.886×10^{-6} kg m s^{-2} was applied for the tube.

Microanalyses were performed by Mr W.T. Hemsted, in the School of Chemistry at the University of Cape Town. Melting ranges were determined on a Kofler hotstage microscope (Reichert Thermovar) and are uncorrected.

Photochemical reactions were performed in an immersion type Hanovia photochemical reactor, under nitrogen.

Reaction of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_3]$ *(1a) with* PPh_3 *(1/2 mol ratio)*

$[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_3]$ (**1a**) (0.60 mmol) was dissolved in THF (10 ml) and PPh_3 (0.60 mmol) added. The mixture was heated under reflux until no further change in the infrared spectrum of the mixture could be detected (in the region 2200–1600 cm^{-1}), then allowed to cool and the solvent removed under reduced pressure. The oily orange residue was extracted with CH_2Cl_2 (5 ml) and the extract chromatographed on an alumina column (made up with 20% ether/hexane). Elution with 20% ether/hexane gave a yellow solution which yielded starting material (23%), on evaporation. An orange band was eluted with 50% ether/hexane, and evaporation under reduced pressure, gave an orange solid. Recrystallisation from ether/pentane gave $[(Cp(CO)(PPh_3)FeC(O)(CH_2)_3Fe(CO)_2(Cp)]$ (**3a**) as a microcrystalline orange solid (64%); m.p: 152–156 °C; $\nu(CO)(CH_2Cl_2)$ 1999(s) 1939(s) 1911(s) 1601(w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.4 (m, 15H) 4.68 (s, 5H) 4.38 (s, 5H) 2.76 (t, J 7 Hz, 2H) 1.26 ppm. (d, J 7 Hz, 4H); Found: C, 63.9; H, 4.9, $C_{35}H_{31}Fe_2O_4P$ calcd.: C, 63.8; H, 4.7%.

Reactions of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n](n = 3\text{–}7)$ *(1a–1e) with tertiary phosphines (1/2 mol ratio)*

General procedure. A mixture of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ (0.60 mmol) and the tertiary phosphine (1.20 mmol) in THF (10 ml) was heated under reflux. The reaction was monitored by IR spectroscopy in the region 2200–1600 cm^{-1}. Heating was continued until no further change in the infrared spectrum of the mixture could be detected. The mixture was then allowed to cool and the solvent removed under reduced pressure. The oily orange residue was extracted with $CHCl_3$ (5 ml) and the extract chromatographed on an alumina column (made up with 20% ether/hexane). Any starting material was eluted with 20% ether/hexane. Elution with 30% ether/hexane separated two bands. An orange band eluted with 50% ether/hexane gave a trace of an orange solid, which, on evaporation was identified as the monoacyl product (3) from its IR spectrum. A second orange band was eluted with ether, and on evaporation an orange solid was isolated; recrystallisation from ether/pentane gave $[FeCp(CO)(PR_3)\{CO(CH_2)_nCO\}Fe(CO)(PR_3)(Cp)]$ as a microcrystalline orange solid.

The reaction times and product yields for the various tertiary phosphine reactions performed are listed in Table 1. The melting points and elemental analyses of the products are given in Table 2 and IR and ^1H NMR data in Table 3.

Attempted decarbonylation of $[(Cp)(CO)(PPh_3)Fe[CO(CH_2)_nCO]Fe(CO)(PPh_3)(Cp)]$ *(n = 4, 6) (**4b** and **4d**)*

(1) By photolysis. A solution of **4b** (5 mmol) in THF (40 ml) was irradiated at 35 °C and the reaction monitored by infrared spectroscopy (in the region 2100–1500 cm^{-1}). The reaction was stopped when the band at 1913 cm^{-1}, due to the starting diacyl compound, had disappeared (3 h). The reaction mixture was filtered under N_2 to remove a brown insoluble solid and the solvent removed from the filtrate under reduced pressure. The brown residue was extracted with 10% CH_2Cl_2/hexane and the extract chromatographed on an alumina column (made up with hexane). Three bands were separated. A yellow band eluted with hexane gave an orange solid with no carbonyl bands, which was identified by ^1H NMR spectroscopy as ferrocene. A red band eluted with 30% CH_2Cl_2/hexane gave $[CpFe(CO)_2]_2$ on evaporation

[ν(CO) 1991(s), 1950(vs, 1778(s) cm^{-1}] A second yellow band was eluted with CH_2Cl_2 and removal of the solvent under reduced pressure gave a yellow oil. The infrared spectrum of this portion showed the presence of some of the starting diacyl compound [ν(CO(CH$_2$Cl$_2$) 1913(s), 1602(w) cm^{-1}]. A strong band at 1732 cm^{-1}; which is in the range for a ν(CO) of an organic ketone or acid, was also observed. The infrared spectrum of the oil in the range 3600–600 cm^{-1} was found to be very similar to that reported for $HOOC(CH_2)_4COOH$ [42].

Similar results were obtained for the photolysis of **4b** in petroleum ether, and in THF, in the presence of PPh_3.

Photolysis of **4d** was carried out in the same way. After irradiation for 3 h the mixture was worked up as described above. A red band was eluted with 30% CH_2Cl_2/hexane and the red solid, obtained on evaporation was identified as $[CpFe(CO)_2]_2$ on the basis of its infrared spectrum (38% yield). A pale yellow band eluted with CH_2Cl_2, gave a yellow oil on evaporation, the infrared spectrum of which was similar to that of $HOOC(CH_2)_6COOH$ (3600–600 cm^{-1}) [42].

(2) Reaction of $[Cp(CO)(PPh_3)Fe[CO(CH_2)_4CO]Fe(PPh_3)(CO)Cp]$ *(**4b**) with* $[RhCl(PPh_3)_3]$. A mixture of (**4b**) (0.5 mmol) and $[RhCl(PPh_3)_3]$ (1.0 mmol) in benzene (5 ml) was stirred at room temperature for 10 h. The mixture was then evaporated under reduced pressure, the red residue extracted with CH_2Cl_2 (5 ml), and the extract chromatographed on an alumina column (made up with 50% CH_2Cl_2/hexane). Only one band was collected on elution with CH_2Cl_2, and evaporation of the solution gave an orange solid identified, by its infrared spectrum as starting material **4b** (98% yield). The solid residue remaining after CH_2Cl_2 extraction for chromatography contained $[RhCl(PPh_3)_3]$.

Photochemical reaction of $[(Cp)(CO)_2FeC(O)(CH_2)_4C(O)Fe(CO)_2(Cp)]$ *(**4b**) with* PPh_3

A mixture of **4b** (0.5 mmole) and PPh_3 (1.0 mmole) in THF was irradiated at 25 ° C for 3 h. The mixture was then filtered to remove a brown insoluble solid, and evaporated under reduced pressure. Chromatography of the brown residue on an alumina column made up with 50% CH_2Cl_2/hexane separated two bands. A red band was eluted with 30% CH_2Cl_2/hexane and, on evaporation, gave $[CpFe(CO_2]_2$ (47% yield). Elution with CH_2Cl_2 gave a pale yellow solution and, on evaporation, a yellow oil was isolated. The IR spectrum of this portion showed it to contain an organic product similar to that observed in the photolysis of **4b**.

Photochemical reaction of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$ *(**1b**) with* PPh_3

A stirred solution of **1b** (3.7 mmol) and PPh_3 (7.6 mmol) in THF (100 ml) was irradiated under N_2 at 30 ° C for 3 h. The reaction was monitored by IR spectroscopy in the region 2100–1500 cm^{-1} and was stopped when no further increase in the product band at 1905 cm^{-1} could be detected. The mixture was evaporated under reduced pressure, the brown residue extracted with CH_2Cl_2 (5 × 20 ml), and the extract filtered under N_2 to remove an insoluble non-carbonyl product. The resulting dark orange solution was concentrated and then chromatographed on an alumina column (made up with petroleum ether b.p. 30–40 ° C). Four bands were separated by elution with petroleum ether and CH_2Cl_2. A yellow band was eluted with petroleum ether and evaporation of the solution yielded an orange solid, the infrared spectrum of which was identical to that reported for $[CpFe(CO)(PPh_3)H]$.

The assignment of this formula to the product was confirmed by the observed reaction of the product with $CHCl_3$ to give green crystals of [CpFe(CO)(PPh_3)Cl].

A second yellow band was eluted with 10% CH_2Cl_2/petroleum ether and evaporation gave an orange solid showing one strong carbonyl band at 1906 cm^{-1} (in CH_2Cl_2). This product was unstable and decomposed rapidly both in solid and in solution on exposure to air, and was not characterised further. A red band eluted with 30% CH_2Cl_2/petroleum ether gave a red solid on evaporation, identified as $[CpFe(CO)_2]_2$ by IR spectroscopy (28%).

Elution with CH_2Cl_2 gave a yellow solution which yielded **4b** (16%) (IR ν(CO); 1913(s) 1604(w) cm^{-1}).

Reactions of $[CpFe(CO)_2]_2[\mu\text{-}CH_2)_n]$ (n = 3, 4 (1a and 1b) with halogens

General procedure. $[CpFe(CO)_2]_2[\mu\text{-}CH_2)_n]$ (0.2 mmole) was dissolved in THF or CH_2Cl_2 (5 ml) and X_2 (X = I or Br) was added with stirring at 20 °C (for I_2) or 0 °C (for Br_2). The mixture was stirred at the addition temperature for 10 min then evaporated under reduced pressure. The brown residue was extracted with CH_2Cl_2 and chromatographed on an alumina column (made up with hexane). Elution with CH_2Cl_2/hexane separated the reaction products. The eluted solutions were evaporated under reduced pressure and the products identified by comparison with authentic samples or by use of published spectral data.

(a) Reactions of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_3]$ (1a) with X_2 (1/2). Addition of I_2 (0.4 mmol) to a solution of **1a** (0.2 mmol) in THF at 20 °C gave a dark brown solution. Work-up as described above separated two products. A pale yellow band, eluted with 20% CH_2Cl_2/hexane, gave a yellow oil on evaporation. The IR and mass spectra of this portion showed that it contained mainly $I(CH_2)_3I$ with a trace of starting material **1a**. A brown band was eluted with CH_2Cl_2 and evaporation of this solution produced a dark purple solid, the IR and ^1H NMR spectra of which were identical to those reported for $[CpFe(CO)_2I]$ [36] (92% yield).

$[CpFe(CO)_2I]$ and $I(CH_2)_3I$ were also isolated from the reaction of **1a** with I_2 in CH_2Cl_2.

The reaction of **1a** with Br_2 in THF was carried out in the same way, and work-up separated two products, which were identified on the basis of their IR, ^1H NMR and mass spectra as $Br(CH_2)_3Br$ and $[CpFe(CO)_2Br]$ (yield 89%).

The reaction of **1a** with Br_2 was also performed at 0 °C in THF. The infrared spectrum of the reaction mixture showed the presence of a cationic product ((ν(CO) 2080(s), 2046(s) cm^{-1}), but this was not isolated.

(b) Reaction of $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_4]$ (1b) with X_2 (1/2). I_2 (0.4 mmol) was added to a stirred solution of **1b** in THF at 20 °C. The mixture was worked up as described above and three products separated. A yellow band eluted with hexane and evaporation left a yellow oil, which was found to contain $I(CH_2)_4I$ and a small amount of $[CpFe(CO)_2\{(CH_2)_4I\}]$ on the basis of the IR and mass spectra of this portion. A brown band was eluted with CH_2Cl_2 and the brown solid produced on evaporation was identified by its IR, ^1H NMR and, mass spectra as $[CpFe(CO)_2I]$ (78%). A brown residue remained after the extraction with CH_2Cl_2 for chromatography, and this was dissolved in a minimum of THF and CH_2Cl_2 was added. The dark red solid which separated was filtered off under suction (0.06 g). This product (**8**) was unstable even in solid form and was only characterised by IR and ^1H NMR spectroscopy. The spectral data are consistent with the structure $[(Cp)(CO)_2$-Fe-

$(CH_2)_4Fe(CO)_2(Cp)]^+[I_2]^-$; ν(CO) (THF) 2080(s), 2046(s) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 4.04 (s, 8 H) δ 5.96 ppm (s, 10 H).The reaction of **1b** with Br_2 was carried out in the same way. The products isolated by chromatography were identified on the basis of their IR, ^{1}H NMR and mass spectra as $Br(CH_2)_4Br$, $[CpFe(CO)_2Br]$ (72%) and $[CpFe(CO)_2\{CH_2)_4Br\}]$ (trace). An orange-brown solid was isolated from the residue remaining after CH_2Cl_2 extraction for chromatography (0.08 g). This was assigned the structure $[(Cp)(CO)_2Fe(CH_2)_4Fe(CO)_2(Cp)]^+$-$[Br_2]^-$, which is consistent with its IR and ^{1}H NMR spectra and its measured paramagnetic susceptibility; ν(CO) (THF) 2076(s) 2040(s) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 4.08 (s, 8H), δ 6.00 (s, 10H); χ_m 6.6 $\times 10^{-7}$ m^3 kg^{-1} at 17°C.

*(c) Reaction of $[CpFe(CO)_2]_2[\mu$-$(CH_2)_4]$ (**1b**) with X_2 (1/1).* I_2 (0.2 mmol) was added to a stirred solution of **1b** in THF (5 ml) at 20°C. After 10 min stirring, the reaction mixture was worked up as described above. A yellow band was eluted with hexane, and evaporation gave an oily yellow solid. IR and ^{1}H NMR spectra showed that this portion contained $I(CH_2)_4I$ and the starting material. The solid was dissolved in a minimum of hexane and on cooling, yellow crystals of **1b** precipitated from the solution (yield, 47%). A brown band was eluted with CH_2Cl_2 and removal of the solvent gave a dark purple solid identified on the basis of IR and ^{1}H NMR spectra as $[CpFe(CO)_2I]$ (36%).

*Reactions of $[CpW(CO)_3]_2[\mu$-$(CH_2)_n]$ (n = 3–5) (**2a–2c**) with tertiary phosphines*

General procedure. $[CpW(CO)_3]_2[\mu$-$(CH_2)_n]$ was dissolved in THF or DME (10 ml) and a two molar equivalent of tertiary phosphine were added. The mixture was heated under reflux and the reaction monitored by IR spectroscopy in the region 2100–1550 cm^{-1}. The reaction was stopped when no further decrease in the carbonyl bands of the starting material could be detected. The mixture was then evaporated under reduced pressure and the residue extracted with ether and chromatographed on an alumina column (made up with 20% ether/hexane). Separation of the products was achieved by elution with increasing concentrations of ether in hexane. The eluted solutions were evaporated under reduced pressure to give the solid products.

*(a) Reaction of **2b** with $PMePh_2$.* A mixture of **2b** (0.3 mmol) and $PMePh_2$ (0.6 mmol) in THF was heated under reflux for 70 h. The mixture was worked up as described above. Elution with 50% ether/hexane gave a pale yellow solution, which yielded a yellow solid on evaporation. The IR and ^{1}H NMR spectra of this portion showed it to contain starting material **2b** (ν(CO) 2009(s) 1910(vs); ^{1}H NMR ($CDCl_3$) δ 5.32 (s, C_5H_5) 1.236(s, $(CH_2)_4$)] and a non-acyl phosphine-substituted product, possibly $[CpW(CO)_2(PPh_2Me)]_2[\mu$-$(CH_2)_4]$ (ν(CO) (CH_2Cl_2) 1923(m, sh), 1945(s); ^{1}H NMR ($CDCl_3$) δ 4.75 (s, J 2 Hz, C_5H_5) 2.18 (d, J 9 Hz, PMe)). A second yellow band was eluted with ether, and evaporation gave a yellow solid which was recrystallised from ether/pentane to give yellow crystals of $[(Cp)(CO)_2(PMePh_2)W\{CO(CH_2)_4CO\}W(PMePh_2)(CO)_2(Cp)]$ (**6a**) (0.17 g, 55%); m.p. 175–179°C; ν(CO) benzene 1923(m), 1840(s), 1611(w) cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 1.25 (m, 4H), 2.30 (d, J 9 Hz, 6 H) 2.84 (t, J 6 Hz, 4H) 5.01 (d, J 1.5 Hz, 10 H) 7.4 (m, 20 H); Found: C, 49.2; H, 3.9. $C_{46}H_{44}O_6P_2W_2$ calcd.: C, 48.9; H, 3.9%.

The reaction of **2b** with PPh_2Me was also carried out in refluxing DME for 38 h. Work up gave **6a** in 54% yield and a yellow solid containing a mixture of starting material and a non-acyl phosphine substituted product. After prolonged heating of a mixture of **2b** and PPh_2Me in DME (72 h), the ^{1}H NMR of the reaction mixture showed an increase in the proportion of the non-acyl product formed, and the diacyl compound **6a** was isolated in only 36% yield.

(b) Reaction of $[CpW(CO)_3]_2[\mu\text{-}(CH_2)_5]$ (2c) with $PMePh_2$. A mixture of **2c** (0.35 mmol) and $PMePh_2$ (0.7 mmol) in THF was heated under reflux for 72 h. Work-up revealed two product bands. A yellow band eluted with 50% ether/hexane gave a yellow solid on evaporation, which on the basis of its IR and ^{1}H NMR spectra was judged to contain a mixture of starting material, a non-acyl phosphine substituted product, and possibly the mono-acyl species $[(Cp)(CO)_2(PMePh_2)W\text{-}\{CO(CH_2)_5\}W(CO)_3(Cp)]$ (**5a**); ν(CO) (CH_2Cl_2) 2008(m), 1924(sh), 1916(s), 1836(vs), 1598(w) cm^{-} ^{1}H NMR ($CDCl_3$) δ 5.32(s, C_5H_5 of **2c**), 5.05 (d, J 2 Hz, C_5H_5 of acyl product), 4.80 (d, J 2 Hz, C_5H_5 of non-acyl product).

A second yellow band was eluted with ether, and evaporation of the yellow solution gave $[(Cp)(CO)_2(PMePh_2)W(CO(CH_2)_5CO]W(PMePh_2)(CO)_2(Cp)]$ (**6b**) as a yellow solid (0.16 g, 54%); m.p. 75–80 ° C; ν(CO) (CH_2Cl_2) 1925(m), 1838(vs), 1596(w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (m, 6H) 2.34 (d, J 9 Hz, 6H) 2.9 (t, J 7 Hz, 4H) 5.04 (d, J 1.8 Hz, 10H) 7.5 (m, 20H); Found: C, 49.7; H, 4.1. $C_{47}H_{46}O_2W_2$ calcd.: C, 50.2; H, 4.3%.

(c) Reaction of $[CpW(CO)_3]_2[\mu\text{-}(CH_2)_4]$ (2b) with PPh_3. A mixture of **2b** (0.3 mmol) and PPh_3 (0.6 mmol) in DME was heated under reflux for 34 h. Two product bands were isolated on chromatographic work up. A yellow band eluted with 50% ether/hexane gave a yellow solid which was found to contain a mixture of **2b**, and a non-acyl substituted product on the basis of the IR and ^{1}H NMR spectra; ν(CO) (CH_2Cl_2) 2008(s), 1924(sh), 1911(vs), 1842(m) cm^{-1}. The ^{1}H NMR spectrum showed a singlet at δ 5.32 (C_5H_5 of **2b** and a doublet at 4.80 (J 1.5 Hz, C_5H_5 for non-acyl product). A second yellow band was eluted with 80% ether/hexane and on evaporation gave a yellow solid, which was formulated as $[(Cp)(CO)_2(PPh_3)WC(O)\text{-}(CH_2)_4W(CO)_3(Cp)]$ (**5b**) (28% yield) on the basis of its IR and ^{1}H NMR data; ν(CO) (CH_2Cl_2) 2006(s), 1924(s), 1910(vs), 1842(s), 1595(w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 15H) 5.32 (s, 5H) 5.05 (s, 5H) 2.92 (t, J 7 Hz, 2H) 1.26 ppm (s, 6H).

The reaction of **2b** with PPh_3 was also carried out in refluxing THF for 75 h. Work-up revealed two product bands. A yellow band was eluted with 50% ether/hexane and judged to contain starting material **2c** (38%) on the basis of the IR and ^{1}H NMR spectra. A second yellow band was eluted with ether, and evaporation under reduced pressure. yielded $[(Cp)(CO)_2(PPh_3)WC(O)(CH_2)_5C(O)W(CO)_2(PPh_3)(Cp)]$ (**6d**) as a yellow solid (45%); ν(CO) (CH_2Cl_2) 1930(m), 1845(vs), 1595(m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.4 (m, 30H) 5.05 (d, J 1.5 Hz, 10H) 2.84 (t, J 7Hz, 4H) 1.26 ppm (m, 6 H); Found: C, 54.5; H, 4.0. $C_{57}H_{50}O_6P_2W_2$ calcd.: C, 54.3; H, 3.9%.

Thermal decarbonylation of the diacyl compounds 6a–6c

General procedure. The diacyl compound was dissolved in DME (5 ml) and an approximate 4-fold excess of tertiary phosphine added. The mixture was heated under reflux for 24 h, allowed to cool, then evaporated under reduced pressure. The ^{1}H NMR of the reaction mixture was recorded and the percentage conversion of the starting material to a non acyl phosphine-substituted product determined from the ratio of the C_5H_5 proton resonances at ca. δ 5.00 and 4.75 for starting material and product, respectively. In each reaction a resonance at ca. δ 5.32 was also observed indicating the presence of some non-substituted $\mu(\alpha,\omega)$-alkanediyl product. For compounds **6a**–**6c** the conversion into non-acyl product was 10, 15, and 50%, respectively.

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References

1 M.H. Chisholm (Ed.), Reactivity of Bridging Hydrocarbyl Ligands, Polyhedron, 7 (1988) no. 10/11.
2 J.R. Moss and L.G. Scott, Coord. Chem. Rev., 60 (1984) 171; C.P. Casey and J.L. Audett, Chem. Rev., 86 (1986) 339.
3 J.D. Scott, M. Crespo, C.M. Anderson and R.J. Puddephatt, Organometallics, 6 (1987) 1772.
4 J.P. Collman, J.I. Brauman and A.M. Madonik, Organometallics, 5 (1986) 218.
5 S.C. Kao, C.H. Thiel and R. Pettit, Organometallics, 2 (1983) 914.
6 J.P. Bibler and A. Wojcicki, J. Am. Chem. Soc., 88 (1966) 4862.
7 G.W. Parshall and J.J. Mrowca, Adv. Organomet. Chem., 7 (1968) 157.
8 S.R. Su and A. Wojcicki, J. Organomet. Chem., 27 (1971) 231.
9 M. Green and D.J. Westlake, J. Chem. Soc. A, (1971) 357.
10 J.W. Faller and A.S. Anderson, J. Am. Chem. Soc., 91 (1969) 1550.
11 B.K. Blackburn, S.G. Davies and M. Whittaker, J. Chem. Soc. Chem. Commun., (1987) 1344.
12 S.G. Davies, I.M. Dordor-Hedgecock, K.H. Sutton and M. Whittaker, J. Am. Chem. Soc., 109 (1987) 5711 and ref. therein.
13 A. Wojcicki, Adv. Organometal. Chem., 11 (1973) 87.
14 S.F. Mapolie, J.R. Moss and L.G. Scott, J. Organomet. Chem., 297 (1985) C1.
15 J.J. Alexander, J. Am. Chem. Soc., 97 (1957) 1729.
16 M.D. Johnson, Acc. Chem. Res., 11 (1978) 57.
17 W.N. Rogers and D.L. Miles, Inorg. Chem., 20 (1981) 3521.
18 T.C. Flood and D.L. Miles, J. Organomet. Chem., 127 (1977) 33.
19 T.G. Attig, R.G. Teller, S.-M. Wu, R. Bau and A. Wojcicki, J. Am. Chem. Soc., 101 (1979) 619.
20 N. Deluca and A. Wojcicki, J. Organomet. Chem., 193 (1980) 359.
21 D. Dong, D.A. Slack and M.C. Baird, Inorg. Chem., 18 (1979) 188.
22 D.A. Slack and M.C. Baird, J. Am. Chem. Soc., 98 (1976) 5539.
23 J.R. Moss, J. Organometal. Chem., 231 (1982) 229.
24 P.K. Monaghan and R.J. Puddephatt, Inorg. Chim. Acta, 76 (1983) L237.
25 J.P. Collman, J.I. Brauman and A.M. Madonik, Organometallics, 5 (1986) 218.
26 J.E. Bercaw, B.J. Burger, and J.R. Moss, to be published.
27 A. Crouch and J.R. Moss, unpublished results.
28 E.J. Kuhlmann and J.J. Alexander, Coord. Chem. Rev., 33 (1980) 195.
29 K.W. Barnett and D.W. Slocum, J. Organomet. Chem., 44 (1972) 1.
30 K.W. Barnett and P.M. Treichel, Inorg. Chem., 6 (1967) 294.
31 A.R. Manning, J. Chem. Soc. A, (1967) 1984.
32 F. Calderazzo, Angew. Chem. Int. Ed. Engl., 16 (1977) 299 and ref. therein.
33 K.W. Barnett, T.G. Pollman and T.W. Soloman, J. Organomet. Chem., 36 (1972) C23.
34 K.W. Barnett, D.L. Beach, S.P. Gaydos and T.G. Pollman, J. Organomet. Chem., 69 (1974) 121.
35 R. Birdwhistell, P. Hackett and A.R. Manning, J. Organomet. Chem., 157 (1978) 239.
36 R.B. King, Organometallic Synthesis, Vol. I: Transition metal compounds, Academic Press, New York and London, 1965.
37 J.R. Moss, L.G. Scott, M.E. Brown and K.J. Hindson, J. Organomet. Chem., 282 (1985) 255.
38 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc., (1966) 1711.
39 H. Adams, N.A. Bailey and M.J. Winter, J. Chem. Soc. Dalton, (1984) 273.
40 L.G. Scott, MSc thesis, University of Cape Town, 1985.
41 F.G. Mann and A.F. Wells, J. Chem. Soc., (1938) 702.
42 C.J. Pouchert, The Aldrich Library of Infrared Spectra, 2nd edit., Aldrich Chemical Co, Wisconsin, 1975.