Journal of Organometallic Chemistry, 394 (1990) 313-327
Elsevier Sequoia S.A., Lausanne
JOM 20797

The synthesis and properties of heterodinuclear alkanediyl complexes of iron(II) containing molybdenum(II), tungsten(II), rhenium(I) and ruthenium(II) *

Holger B. Friedrich, John R. Moss * and Bridget K. Williamson

Department of Chemistry, University of Cape Town, Rondebosch 7700 (South Africa)

(Received January 31st, 1990)

Abstract

The reactions of the iodoalkyl compounds $[(\eta^5\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nI\}]$ with $Na[ML_y]$ yield the new heterodinuclear alkanediyl compounds $[(\eta^5\text{-}C_5R_5)\text{-}(CO)_2Fe(CH_2)_nML_y]$ (where $R = H$: $ML_y = Mo(CO)_3Cp$, $W(CO)_3Cp$, $Re(CO)_5$, $n = 3\text{-}6$; $R = CH_3$: $ML_y = Ru(CO)_2Cp$, $n = 3\text{-}5$; $Re(CO)_5$, $n = 4$). The related mixed ligand complex $[Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp^\star]$ has also been prepared (where $Cp = \eta^5\text{-}C_5H_5$ and $Cp^\star = \eta^5\text{-}C_5(CH_3)_5$). The new compounds have been fully characterised by analytical and spectroscopic methods.

Introduction

Heterobimetallic catalysts have been found to be superior in activity, selectivity, and efficiency to catalysts derived from either of the respective monometallic components. This has resulted in much effort being directed towards the study of heterobimetallic complexes. These complexes could serve as models for catalytic intermediates, as catalyst precursors, or as catalysts themselves [1]. It is also of interest to investigate the effect that one metal has on another when the two metals are in close proximity within the same molecule.

Several strategies have been employed to synthesize heterobimetallic complexes, one of which involves the preparation of compounds with direct metal-metal bonds [2]. Not all metals however will form stable metal-metal bonds, particularly early-late transition metal combinations. Another approach is to prepare compounds where phosphorus and/or arsenic bridging ligands hold the different metal atoms together [3-7]. The presence of phosphorus or arsenic may however be

---

* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

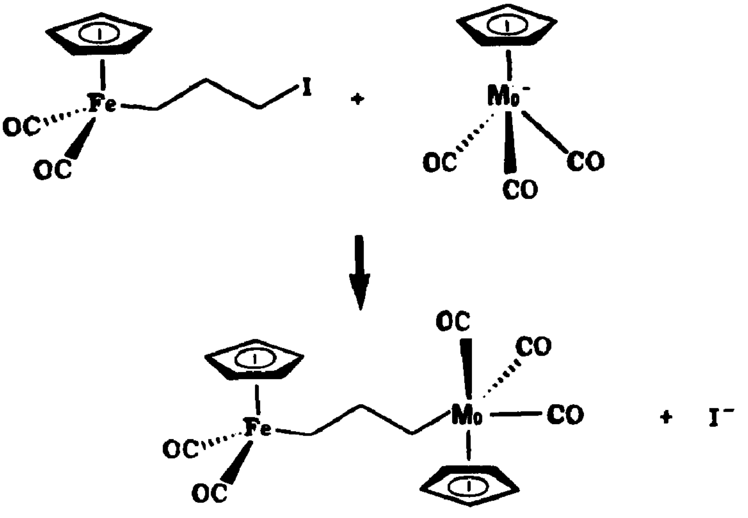
0022-328X/90/$03.50

undesirable if the complex is to be used as a catalyst precursor, since these elements may poison the catalytically active sites.

Since the metal-carbon sigma bond is ubiquitous in organometallic chemistry, we have developed the strategy of building up heterobimetallic complexes in which the metal centres are bridged by an alkanediyl ligand. This method should be widely applicable to a range of heterobimetallic complexes. It has been previously shown that bridging methylene groups can hold two different metals together, for example Ti and Pt [8] or Ta and Pt [9]. Stone and co-workers, in an extensive and important series of papers [10], have demonstrated the wide applicability of using carbene or carbyne bridging ligands for synthesizing many novel heterobimetallic complexes. Several ethylene-bridged complexes of the type $L_xMCH_2CH_2M^1L_y$ have been prepared by the reactions of cationic ethylene complexes with metal carbonyl anions [11,12]. Some years ago the propanediyl complex $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$ ($Cp = \eta^5$-C_5H_5) was prepared by the reaction of $[CpFe(CO)_2\{(CH_2)_3Br\}]$ with $Na[CpMo(CO)_3]$, but the yield was only 18% [13]. Knox and co-workers then demonstrated that the heterobimetallic complex $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ could be obtained in 87% yield by the reaction of the iodoalkyl compound $[CpFe(CO)_2\{(CH_2)_3I\}]$ with $Na[CpRu(CO)_2]$ [14]. This suggested that the use of iodoalkyl complexes might provide a more useful and potentially general high yield route to heterobimetallic alkanediyl complexes. We have examined this possibility and now present our results.

Results and discussion

An initial experiment showed that the iodoalkyl compound $[CpFe(CO)_2\{(CH_2)_3$-$I\}]$ [15] reacts with $Na[CpMo(CO)_3]$ to give good yields of the Fe–Mo heterobimetallic propanediyl compound (Scheme 1). This was subsequently shown to be one



Scheme 1

example of a general route to heterobimetallic alkanediyl complexes, as shown in eqn. 1.

$$[(\eta^5\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nI\}] + Na[ML_y] \rightarrow$$
$$[(\eta^5\text{-}C_5R_5)(CO)_2Fe(CH_2)_nML_y] + NaI \quad (1)$$

where $R = H$, $ML_y = Mo(CO)_3Cp$, $W(CO)_3Cp$ or $Re(CO)_5$, $n = 3\text{–}6$; $R = CH_3$, $ML_y = Ru(CO)_2Cp$, $n = 3\text{–}5$ or $Re(CO)_5$, $n = 4$.

The related mixed ligand complex $[Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp^\star]$ ($Cp^\star = \eta^5\text{-}C_5(CH_3)_5$) was prepared by a similar route. We have also prepared the compounds $[Cp(CO)_2Fe(CH_2)_nRu(CO)_2Cp]$ ($n = 4\text{–}6$) by this route and described the structure of the Fe–Ru hexanediyl compound [16].

The new alkanediyl complexes were obtained in good yield, except for the Fe–Re complexes with $n = 5$ and 6, which were obtained in only 12–14% yield. Highest yields of the Fe–Re compounds were obtained after short reaction times, presumably due to the instability of these compounds in the reaction solution. The alkanediyl complexes were all obtained as yellow crystalline solids, which are stable in air for several days but mildly light sensitive. The complexes are generally stable in solution under nitrogen but decompose when the solutions are exposed to air. The Fe–Re and Fe–Ru complexes are very much more soluble in hexane than the Fe–Mo or Fe–W complexes. The hexane solubility of all the complexes increases with increasing length of the alkyl chain. Yields, microanalyses, IR and other physical data for the new compounds are given in Tables 1 and 2. The IR spectra in the ν(CO) region show the expected number of peaks in the positions expected by comparison with data for the related mononuclear alkyl compounds.

Assignments of the ^1H and ^{13}C NMR data were made by using COSY and HETCOR experiments, as well as by comparison of the data with that for some of their homodinuclear analogues [16–18].

From the ^1H NMR data (Tables 3 and 4) it can be seen that the methylene protons on the carbon α to a metal have a chemical shift that depends on that metal. For example, the protons α to Fe all resonate between 1.40 and 1.50 ppm. Similarly for the compounds with $n = 4\text{–}6$, the β protons have chemical shifts that depend on the associated metal. The β proton peaks of the complexes where $n = 3$ show a significant effect due to both metals on each end of the carbon chain. Thus for the Fe–W complex the chemical shift for the β methylene protons is 1.45 ppm, whilst for the Fe–Mo complex it is 1.71 ppm, and for the Fe–Re complex 1.82 ppm. The δ value of the proton peaks in positions γ to a metal and beyond no longer appear to be affected by the metal. It therefore seems clear that a metal influences the protons in the α and β positions to it and that the effect is no longer apparent for the protons γ to the metal. Also apparent is the approximately 0.5 ppm upfield shift of the peaks due to the protons α to Fe for the $Cp^\star$ complexes relative to those for the analogous Cp complexes. Neither the Cp protons nor the methyl protons of the $Cp^\star$ ligand show any significant shift with change in either the length of the hydrocarbon chain or the metal on the other end of the chain.

From the ^{13}C NMR data (Tables 5 and 6) it can be seen that for the methylene chain of the complexes where $n > 3$, the peaks due to the carbon atom α to a metal appear at positions that depend on that metal. For example, carbon atoms α to Fe resonate at between 3 and 4 ppm, while carbon atoms α to Re resonate at ca. -9

Table 1

Data for $[Cp(CO)_2Fe(CH_2)_nML_y]$

n	ML_y	Rxn time (h)	Yield (%)	M.p. (°C)	IR ν(CO) (cm^{-1}) [a]	Elemental analysis	
						C: found (calcd.)	H: found (calcd.)
3	$CpMo(CO)_3$	73	66	97– 99	2016s, 2005s, 1951s, 1937s, 1925s	[b]	[b]
4	$CpMo(CO)_3$	72	80	110–115	2018s, 2008s, 1954s, 1933vs	48.10(47.70)	4.00(3.77)
5	$CpMo(CO)_3$	120	41	87– 88	2017s, 2008s, 1954s, 1933vs	49.05(48.78)	4.10(4.07)
6	$CpMo(CO)_3$	21	45	56– 59	2018s, 2008s, 1954s, 1933vs	49.50(49.80)	4.30(4.35)
3	$CpW(CO)_3$	120	85	113–115(dec)	2014s, 2006s, 1952s, 1928s, 1921s	39.30(39.14)	2.95(2.90)
4	$CpW(CO)_3$	72	72	143–149(dec)	2016s, 2009s, 1955s, 1925vs	39.35(40.29)	3.20(3.18)
5	$CpW(CO)_3$	67	10	102–104(dec)	2014s, 2008s, 1954s, 1925vs	41.80(41.41)	3.60(3.48)
6	$CpW(CO)_3$	45	40	54– 63	2015s, 2008s, 1954s, 1925vs	42.40(42.46)	3.60(3.73)
3	$Re(CO)_5$	4	69	110–111	2010vs, 1981m, 1954m	33.30(33.02)	2.20(2.02)
4	$Re(CO)_5$	1.75	89	103–104	2010vs, 1981m, 1955m	34.15(34.34)	2.40(2.32)
5	$Re(CO)_5$	5.25	14	57– 59	2010vs, 1982m, 1955m	36.10(35.59)	2.85(2.62)
6	$Re(CO)_5$	19	12	[c]	2009vs, 1981m, 1954s	[d]	[d]

[a] In hexane, m = medium, s = strong, vs = very strong. [b] Data in ref. 13. [c] Waxy solid. [d] Not obtained.

Table 2

Data for [$Cp^{\star}(CO)_2Fe(CH_2)_nML_y$]

n	ML_y	Rxn time (h)	Yield (%)	M.p. (°C)	IR ν(CO) (cm^{-1}) [a]	Elemental analysis		Molecular ion (m/z)
						C: found (calcd.)	H: found (calcd.)	
3	$CpRu(CO)_2$	43	65	99–100	2015s, 1985s, 1957s, 1930s	51.40(51.66)	5.00(5.09)	512
4	$CpRu(CO)_2$	84	34	98–101	2018s, 1987s, 1959s, 1933s	52.40(52.57)	5.40(5.33)	526
5	$CpRu(CO)_2$	45	75	83– 89	2017s, 1987s, 1958s, 1932s	53.40(53.43)	5.70(5.59)	540
4	$Re(CO)_5$	1.75	17	100–102	2008vs, 1986s, 1979s, 1932s	40.10(40.06)	3.80(3.66)	630
3	$CpFe(CO)_2$	5	35	88– 89	2005vs, 1985vs, 1952vs, 1930vs	56.80(56.68)	5.50(5.58)	466

[a] In hexane, s = strong, vs = very strong.

Table 3

^{1}H NMR data for $[Cp(CO)_2Fe(CH_2)_nML_y]$ [a]

n	ML_y	CpM	CpFe	MCH_2	$FeCH_2$	$FeCH_2CH_2$	MCH_2CH_2	$FeCH_2CH_2CH_2$	$MCH_2CH_2CH_2$
3	$CpMo(CO)_3$	5.24s	4.74s	1.62m	1.44m	1.71s			
4	$CpMo(CO)_3$	5.28s	4.72s	1.68s	1.48s	1.48s	1.68s		
5	$CpMo(CO)_3$	5.26s	4.72s	1.60s	1.44s	1.44s	1.60s	1.36s	
6	$CpMo(CO)_3$	5.32s	4.73s	1.60s	1.46s	1.46s	1.60s	1.34s	1.34s
3	$CpW(CO)_3$	5.37s	4.73s	1.58m	1.42m	1.45m			
4	$CpW(CO)_3$	5.34s	4.69s	1.62s	1.48s	1.48s	1.62s		
5	$CpW(CO)_3$	5.35s	4.70s	1.52s	1.42s	1.40s	1.51s	1.30m	
6	$CpW(CO)_3$	5.34s	4.69s	1.51s	1.41s	1.41s	1.51s	1.29s	1.29s
3	$Re(CO)_5$		4.72s	1.00m	1.49m	1.82m			
4	$Re(CO)_5$		4.72s	1.00m	1.50s	1.48s	1.80m		
5	$Re(CO)_5$		4.72s	0.92m	1.44s	1.43s	1.76qn [b]	1.30m	
6	$Re(CO)_5$		4.72s	0.92m	1.42s	1.42s	1.74m	1.28s	1.28s

[a] In $CDCl_3$ relative to TMS (0.00 ppm), s = singlet, qn = quintet, m = multiplet. [b] $J = 7.7$ Hz.

Table 4

^{1}H NMR data for $[Cp^*(CO)_2Fe(CH_2)_nML_y]$ [a]

n	ML_y	$C_5(CH_3)_5$	CpM	MCH_2	Cp^*FeCH_2	$FeCH_2CH_2$	MCH_2CH_2	$FeCH_2CH_2CH_2$
3	$CpRu(CO)_2$	1.72s	5.18s	1.64s	0.91m	1.64s		
4	$CpRu(CO)_2$	1.72s	5.22s	1.67s	0.96m	1.55s	1.55m	
5	$CpRu(CO)_2$	1.72s	5.21s	1.64m	0.90m	1.38m	1.51m	1.30m
4	$Re(CO)_5$	1.72s		0.96m	0.88m	1.48m	1.48m	
3	$CpFe(CO)_2$	1.70s	4.68s	1.46m	0.93m	1.46m		

[a] In $CDCl_3$ relative to TMS (0.00 ppm).

ppm. The α carbon atom peaks are shifted ca. 4–5 ppm downfield for the complexes with $n = 3$. This is presumably due to the influence of the metal on the other end of the chain. The influence of a metal on the chemical shifts of carbon atoms in the methylene chain diminishes along the chain and is thus only really apparent in the α, β and γ positions relative to that metal. As the influence of the second metal decreases and the carbon becomes increasingly influenced by one metal only, the chemical shifts of the carbon atoms move upfield. As has been observed before [15], the peaks of the carbon atoms α to Fe for the Cp* complexes are shifted by ca. 10 ppm downfield relative to those for the Cp complexes. This deshielding effect is no longer apparent for the β-carbon atoms. Neither alkyl chain length nor the nature of the metal on the opposite end of the chain affects the position of the CO, Cp or Cp* peaks.

Mass spectrometry provides the simplest readily available method of unambiguously confirming the composition of these heterodinuclear complexes, since all other data obtained do not completely exclude the possibility of equimolar mixtures of the monodinuclear alkanediyl complexes of the respective transition metals. Thus the heterobimetallic nature of these complexes is confirmed either by the observation of a molecular ion for the proposed structure or fragment ions which are only possible from the heterodinuclear complex. Molecular ions were observed for many of the complexes studied under electron impact conditions, and in all cases where chemical ionization was used.

The major ions observed in the electron impact mass spectra of the compounds, $[Cp(CO)_2Fe(CH_2)_nML_y]$, $n = 3$–6, $ML_y = Mo(CO)_3Cp$, $W(CO)_3Cp$, $Re(CO)_5$, are listed in Table 7. Possible fragmentation sequences giving rise to these ions are shown in Scheme 2.

Because CO and Fe both have masses which are multiples of 14 (the mass of one CH_2 unit) many mass spectral assignments are ambiguous and the exact fragmentation sequence is not certain from the low resolution data obtained. However, often the exact order of fragment loss is not significant and in many cases other data available indicates which of two possible assignments is the more likely.

Ions corresponding to $[Cp_2Fe]^+$ and $[Cp_2M]^+$ are observed in all the spectra. The formation of ferrocene in complexes containing the $[Cp(CO)_2Fe]$ unit has been observed previously [15,19] and it is noteworthy that other metals with Cp ligands in these type of complexes behave similarly. High resolution accurate mass data obtained for the complex $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$ confirm the formation of $[Cp_2Mo]^+$ with a relative abundance of 20%. The ions $[CpM(CO)_x]^+$ (M = Mo, W,

Table 5

^{13}C NMR data for $[Cp(CO)_2Fe(CH_2)_nML_y]$ [a]

n	ML_y	$MCO_{(trans)}$ [b]	$MCO_{(cis)}$ [b]	FeCO	CpM	CpFe	MCH_2	$FeCH_2$	β-Fe [c]	β-M [d]	γ-Fe	γ-M
3	$CpMo(CO)_3$	240.0	227.7	217.7	92.7	85.2	6.4	8.4	45.5			
4	$CpMo(CO)_3$	235.0	227.1	217.3	92.6	85.1	2.8	3.3	42.0 [e]	44.4 [e]		
5	$CpMo(CO)_3$	239.9	227.7	217.7	92.7	85.3	3.0	3.8	38.1	36.4	40.8	
6	$CpMo(CO)_3$	239.9	227.7	217.8	92.7	85.3	2.8	3.7	38.3	36.5	34.3	35.1
3	$CpW(CO)_3$	229.1	217.4 [e]	217.6 [e]	91.4	85.2	−5.7	9.1	45.8			
4	$CpW(CO)_3$	[f]	218.1 [e]	217.8 [e]	92.1	85.8	−9.1	3.9	42.4 [e]	45.3 [e]		
5	$CpW(CO)_3$	[f]	217.5 [e]	217.7 [e]	91.5	85.3	−9.6	3.8	38.0	36.9	41.2	
6	$CpW(CO)_3$	[f]	217.5 [e]	217.8 [e]	91.5	85.3	−9.8	3.7	38.3	37.0	34.2	35.6
3	$Re(CO)_5$	181.4	186.1	217.2		85.0	−3.9	11.4	48.3			
4	$Re(CO)_5$	181.4	185.9	217.5		85.3	−9.0	3.3	46.4	44.5		
5	$Re(CO)_5$	181.6	186.1	217.8		85.3	−8.9	4.0	37.8	39.0	42.8	
6	$Re(CO)_5$	181.5	186.0	217.7		85.3	−9.1	3.8	38.3	39.2	34.2	37.1

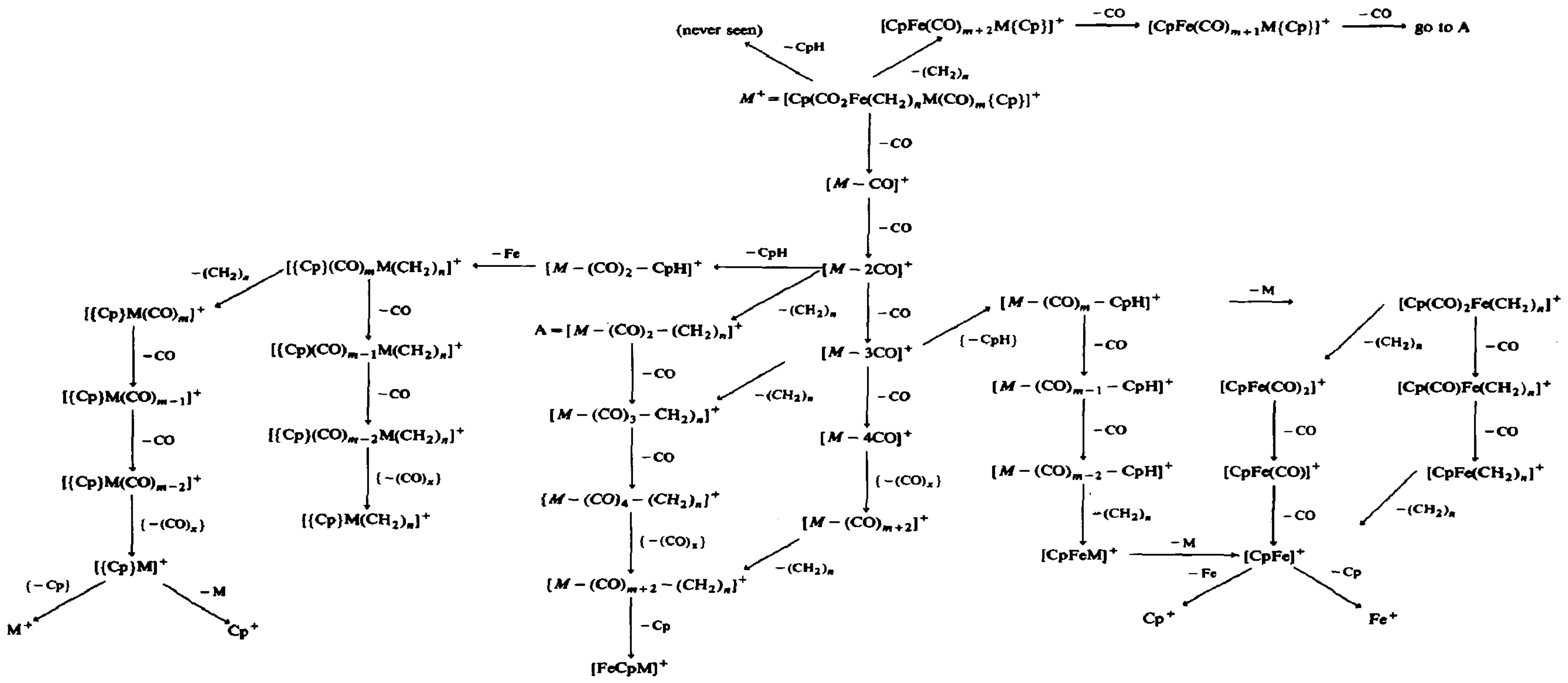
[a] In $CDCl_3$ relative to TMS (0.00 ppm). [b] Relative to the alkyl chain. [c] β-Fe refers to the carbon atom of the alkyl chain β to Fe etc. [d] β-M refers to the carbon atom of the alkyl chain β to M etc. [e] Assignments could be interchanges. [f] Not observed.

Table 6

^{13}C NMR data for $[Cp^*(CO)_2Fe(CH_2)_nML_y]$ [a]

n	ML_y	MCO	Cp^*FeCO	CpM	$C_5(CH_3)_5$	MCH_2	$FeCH_2$	β-Fe	β-M	γ-Fe	$C_5(CH_3)_5$
3	$CpRu(CO)_2$	202.7	219.7	88.5	94.7	2.6	18.2	48.3			9.4
4	$CpRu(CO)_2$	202.5	219.6	88.5	94.7	−2.9	13.9	43.4	46.4		9.3
5	$CpRu(CO)_2$	202.5	219.7	88.6	94.7	−2.8	14.3	37.6	39.9	41.1	9.3
4	$Re(CO)_5$	186.2 [b], 181.7 [c]	219.7		94.7	−8.7	13.5	46.0	45.4		9.3
3	$CpFe(CO)_2$	217.9	219.6	85.2	94.7	9.4	18.3	46.9			9.4

[a] In $CDCl_3$ relative to TMS (0.00 ppm). [b] CO is in *cis* position. [c] CO is in *trans* position relative to alkyl chain.



Scheme 2. Illustration of possible mass spectral fragmentations giving rise to ions observed. {Cp} applicable only to Mo and W; (CH$_2$)$_n$ may be lost as a complete unit or in increments; {−(CO)$_x$} applicable to Re where further CO loss may occur.

Table 7

Major ions observed in electron impact mass spectra of $[Cp(CO)_2Fe(CH_2)_nML_y]$ [a]

Ion (singly charged positive)	Relative intensity of ion (% of base peak)											
	$M = Cp(CO)_2Fe(CH_2)_nMo(CO)_3Cp$				$M = Cp(CO)_2Fe(CH_2)_nW(CO)_3Cp$				$M = Cp(CO)_2Fe(CH_2)_nRe(CO)_5$			
	3	4	5	6	3	4	5	6	3	4	5	6
M	<1	0	(CI)	(CI)	2	0	(CI)	(CI)	8	4	(CI)	(CI)
$M-(CH_2)_n$	1	0	0	0	0	0	0	<1 [b]	2	2 [b]	0	1 [b]
$M-CO$	1	1	<1	<1	0	0	0	0	1	2	0	<1
$M-2CO$	<1	0	<1	0	3	0	0	<1	3	2	<1	2
$M-3CO$	<1	0	<1	0	2	0	0	<1	1	44 [b]	<1	1
$M-4CO$	<1	1	<1	<1	2	0	0	<1	3	10 [b]	<1	1 [b]
$M-5CO$	2	3	3	<1	5	5	0	<1	2	8 [b]	<1	<1
$M-6CO$	–	–	–	–	–	–	–	–	2	17 [b]	<1	<1
$M-7CO$	–	–	–	–	–	–	–	–	4	10 [b]	<1	1
$M-2CO-(CH_2)_x$	Ion intensity ≤1% except for ions also representing $[M-(CH_2)_n-(CO)_x]^+$											
$M-(CH_2)_n-CO$	1	0	0	<1	2	0	0	<1	25	44	3	1
$M-(CH_2)_n-2CO$	2	1	0	<1	5	0	0	<1	4	10	<1	<1
$M-(CH_2)_n-3CO$	3	3	0	0	10	5	<1	1	4	8	1	<1
$M-(CH_2)_n-4CO$	2	3	0	1	12	7	1	1	30	17	4	1
$M-(CH_2)_n-5CO$	10	15	15	2	21	15	5	5	16	10	5	1
$M-(CH_2)_n-6CO$	–	–	–	–	–	–	–	–	8	8	4	<1
$M-(CH_2)_n-7CO$	–	–	–	–	–	–	–	–	4	4	2	1
$M-2CO-CpH$	0	0	1	0	0	5	1	2	9	2	<1	1
$M-3CO-CpH$	1	1	1	1	10	5	4	4	2	10	2	<1
$M-4CO-CpH$ [c]	5	17	10	<1	15	35	6	3	4	20	6	1
$M-5CO-CpH$	10	0	10	3	8	20	8	5	3	10	3	<1
$M-6CO-CpH$	–	–	–	–	–	–	–	–	3	4	1	<1
$M-7CO-CpH$	–	–	–	–	–	–	–	–	4	2	1	<1

$M-2CO-CpH-(CH_2)_x$	Ion intensity ≤10% except for values corresponding to above ions											
$M-Cp(CO)_2Fe-(14)_2$ [d]	10	30	20	3	8	10	5	0	10	50	<1	<1
$M-Cp(CO)_2Fe-(14)_3$	10	0	1	<1	21	4	2	0	35	0	1	0
$M-Cp(CO)_2Fe-(14)_4$	6	15	0	1	10	50	1	4	10	62	<1	<1
$M-Cp(CO)_2Fe-(14)_5$	10	0	5	<1	12	0	4	0	15	0	6	0
$M-Cp(CO)_2Fe-(14)_6$	5	25	5	5	8	15	8	8	3	25	<1	2
$M-Cp(CO)_2Fe-(14)_7$	10	5	5	2	8	0	6	0	10	0	6	0
$M-Cp(CO)_2Fe-(14)_8$	10	15	0	5	6	15	3	10	3	15	0	2
$M-Cp(CO)_2Fe-(14)_9$	20	10	30	1	12	3	10	0	5	0	5	0
$M-Cp(CO)_2Fe-(14)_{10}$	–	35	1	5	–	40	4	10	2	5	0	2
$M-Cp(CO)_2Fe-(14)_{11}$	–	–	30	4	–	–	10	0	2	0	3	0
$M-Cp(CO)_2Fe-(14)_{12}$	–	–	–	30	–	–	–	12	2	2	<1	<1
$M-Cp(CO)_2Fe-(14)_{13}$	–	–	–	–	–	–	–	–	4	1	<1	0
$M-Cp(CO)_2Fe-(14)_{14}$	–	–	–	–	–	–	–	–	–	3	1	<1
$M-Cp(CO)_2Fe-(14)_{15}$	–	–	–	–	–	–	–	–	–	–	0	0
$M-Cp(CO)_2Fe-(14)_{16}$	–	–	–	–	–	–	–	–	–	–	–	<1
$[MC_3H_3]$	5	6	5	10	3	5	3	3	3	2	1	<1
$Cp(CO)_2Fe(CH_2)_n$	5	0	0	0	5	5	2	2	1	0	0	<1
$Cp(CO)_2Fe(CH_2)_n-(14)_2$ [e]	0	0	0	3	3	0	0	0	1	0	0	0
$Cp(CO)_2Fe(CH_2)_n-(14)_3$	10	20	20	2	50	25	100	100	5	31	32	7
$Cp(CO)_2Fe(CH_2)_n-(14)_4$	15	2	10	3	32	0	2	0	12	0	1	0
$Cp(CO)_2Fe(CH_2)_n-(14)_5$	5	40	20	1	45	40	20	14	30	40	16	2
$Cp(CO)_2Fe(CH_2)_n-(14)_6$	15	1	65	0	28	0	40	0	20	1	23	0
$Cp(CO)_2Fe(CH_2)_n-(14)_7$	2	48	1	8	4	30	1	40	5	36	1	14
$Cp(CO)_2Fe(CH_2)_n-(14)_8$	100	12	42	1	100	4	40	2	100	4	38	0
$Cp(CO)_2Fe(CH_2)_n-(14)_9$	–	100	6	15	–	100	1	36	–	100	3	28
$Cp(CO)_2Fe(CH_2)_n-(14)_{10}$	–	–	100	0	–	–	69	3	–	–	100	6
$Cp(CO)_2Fe(CH_2)_n-(14)_{11}$	–	–	–	100	–	–	–	68	–	–	–	100

(continued)

Table 7 (continued)

Ion (singly charged positive)	Relative intensity of ion (% of base peak)											
	$M = \mathrm{Cp(CO)_2Fe(CH_2)}_n\mathrm{Mo(CO)_3Cp}$				$M = \mathrm{Cp(CO)_2Fe(CH_2)}_n\mathrm{W(CO)_3Cp}$				$M = \mathrm{Cp(CO)_2Fe(CH_2)}_n\mathrm{Re(CO)_5}$			
	3	4	5	6	3	4	5	6	3	4	5	6
$[\mathrm{FeC_3H_3}]$	10	17	16	20	8	8	8	8	8	9	12	13
Fe	50	60	60	70	27	30	67	54	27	27	55	73
M	10	4	5	15	0	0	0	0	4	3	0	<1
$\mathrm{Cp_2Fe}$	40	33	30	18	17	25	18	13	26	16	34	2
$\mathrm{Cp_2M}$	20	21	55	6	15	15	16	9	–	–	–	–
FeCpM	Equivalent to $[\mathrm{CpM(CO)_2}]^+$				Equivalent to $[\mathrm{CpM(CO)_2}]^+$				5	5	3	0

[a] $(\mathrm{CH_2})_x$: $2 \leqslant x \leqslant n$, $(\mathrm{CO})_x$: $x = 1$–5, M = Mo, W; $x = 7$, M = Re. (CI): molecular ion evident in chemical ionization spectrum only, –: ion not applicable to this complex. Ion intensity listed is that of the most abundant isotope combination. [b] Ion has more than one possible assignment: another assignment is more probable. [c] $[M - 4\mathrm{CO} - \mathrm{CpH}]^+$ is numerically equivalent to $[M - \mathrm{Cp(CO)_2FeH}]^+$. [d] Ions at these masses could be due to any appropriate combination of losses of $\mathrm{CH_2}$ and CO; the final species after the series of losses in $[\mathrm{CpM}]^+$. [e] Ions at these masses could be due to any appropriate combination of losses of $\mathrm{CH_2}$ and CO; the final species after the series of losses is $[\mathrm{CpFe}]^+$.

$x = 0$–3) are relatively abundant as are the ions [$CpFe(CO)_x$] ($x = 0$–2). [$CpFe$]$^+$ (m/z 121) is the base peak in all these spectra except for the Fe–W complexes where $n = 5$ or 6 where it is [$CpFe(CO)_2(CH_2)_n - C_3H_6$]$^+$. The ion due to the free metal species is always observed for Fe (25–70%), Mo (4 and 15%), Re (less than 5%), and is never seen for W.

Ions involving metal–metal bonding after loss of the polymethylene bridge are relatively abundant, even though the expected precursor, [$Cp(CO)_2FeML_y$]$^+$ (M = Mo, W, $L_y = Cp(CO)_3$; M = Re, $L_y = (CO)_5$) is only observed unambiguously in the cases when $n = 3$ and M = Mo, Re. This indicates a stronger interaction between Fe and the metal atom at the other end of the carbon chain for shorter chain complexes, as was observed in the mass and NMR spectra of the complexes [$Cp(CO)_2Fe(CH_2)_nX$] with $n = 3$–10, X = I, Br [15].

The relative abundance of the ion [$CpFeMCp$]$^+$ (M = Mo and W) or [$CpFeRe$]$^+$ highest for $n = 3$, and decreases as n is increased to 6. The presence of both [$CpFeM$]$^+$ and [$CpM(CO)_2$]$^+$, which have the same nominal mass, is indicated by the accurate mass data obtained for m/z 219 in the complex [$Cp(CO)_2Fe(CH_2)_3$-$Mo(CO)_3Cp$]. These data show that both the species [$CpFeMo$]$^+$ and [$CpMo(CO)_2$]$^+$ are present, with relative abundances 0.2% and 9% respectively. In the case of Re, the ions observed at m/z 308 must be due to [$CpFeRe$]$^+$, as [$CpRe(CO)_2$]$^+$ would unlikely to be present. In none of the spectra is the ion corresponding to [FeM]$^+$ observed, except possibly in the case of Re, where that peak may also be assigned to [$Re(CO)_2$]$^+$.

The loss of C_5H_5 (65 dalton) is not usually observed in the mass spectral fragmentation of the compounds. In contrast, the loss of C_5H_6 (66 dalton) does seem to occur, not from the molecular ion itself, but after the initial loss of, e.g., 2 or more carbonyls from the molecular ion.

Conclusions

We have shown that good yields of heterobimetallic alkanediyl compounds can be obtained by reactions of the iodoalkyl iron compounds [$CpFe(CO)_2\{(CH_2)_nI\}$] with several metal carbonyl anions. In complexes with a shorter alkanediyl chain length the data obtained imply a degree of intermetallic interaction. We are at present investigating the reactivity of these compounds. These studies will give further information about the effect that one metal has on another when the two are in close proximity in the same molecule. Initial results show, for example, that some reactions are totally metalloselective.

Experimental

All reactions were carried out under nitrogen by standard Schlenk tube techniques. Tetrahydrofuran (THF) was distilled from sodium. Alumina (BDH, active neutral, Brockman grade 1) was deactivated before use. Melting points were recorded on a Kofler hot-stage microscope (Reichert Thermovar) and are uncorrected. The [$CpFe(CO)_2\{(CH_2)_nI\}$] complexes were prepared by a published procedure [15]. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian XR 200 spectrometer which was also used for the COSY and HETCOR experiments. Mass spectral data were obtained on one of four instruments: (A) a VG micromass 16F magnetic sector spectrometer, (B) a Kratos MS80 RFA double-focussing spectrometer, (C) a Kratos MS50 double-focussing spectrometer and (D) a Finnigan quadrupole spectrometer. Accurate masses were obtained on the Kratos MS80 RFA spectrometer at resolution 10,000 (5% valley definition). Compounds that were examined on more than one system were always found to yield similar mass spectra on all mass spectrometers, and instrumental bias was negligible. All spectra were obtained with a source temperature of < 170 ° C, and with a probe temperature of 40 ° C increased to ca. 150 ° C by approximately 20 ° C per minute. Electron impact spectra were obtained with a beam energy of 70 eV; ion acceleration voltages were 4 kV for instruments (A) and (B) and 8 kV for instrument (C). Chemical ionization was with isobutane as reagent gas on instrument (B), and with methane on instrument (D). CIMS was applied only to compounds for which no molecular ion was seen under electron impact conditions.

Preparation of $[Cp(CO)_2Fe(CH_2)_nML_y]$; $n = 3–6$, $ML_y = Mo(CO)_3Cp$, $W(CO)_3Cp$, $Re(CO)_5$

A solution of the sodium salt of the transition metal anion (1.60 mmol) in THF (9 ml) was added to one of $[CpFe(CO)_2\{(CH_2)_nI\}]$ (1.47 mmol) in THF (6 ml) during 5 minutes with stirring at −78 ° C. The solution was allowed to attain room temperature and stirred until the reaction was complete as judged by monitoring of the ν(CO) region in the IR spectrum. (For reaction times see Table 1.) The solvent was removed under reduced pressure. The crude product was then extracted with CH_2Cl_2, filtered and the solvent removed under reduced pressure. One of the following work-up procedures was used:

For $[Cp(CO)_2Fe(CH_2)_nRe(CO)_5]$, $n = 3–6$. The crude product was dissolved in a minimum of hexane and transferred to an alumina column. Upon elution with hexane a broad yellow band was collected, and this was concentrated and then cooled to −78 ° C. The yellow product separated from this solution. The mother liquor was syringed off and the product dried under reduced pressure.

For $[Cp(CO)_2Fe(CH_2)_nM(CO)_3Cp]$, $M = Mo$, $n = 3, 5, 6$; $M = W$, $n = 5, 6$. The crude product was dissolved in a minimum of CH_2Cl_2 and transferred to an alumina column made up in hexane. Elution with hexane first yielded a pale yellow band which was shown to contain only the $[CpFe(CO)_2\{(CH_2)_nI\}]$ starting material. Further elution with hexane or 5% CH_2Cl_2 in hexane yielded a second, broad, intense yellow band. This band was collected, concentrated and cooled to −78 ° C. The yellow product separated from this solution. The mother liquor was syringed off and the product dried under reduced pressure.

For $[Cp(CO)_2Fe(CH_2)_3W(CO)_3Cp]$ *and* $[Cp(CO)_2Fe(CH_2)_4Mo(CO)_3Cp]$. The product was dissolved in hot hexane, filtered and cooled to −78 ° C. The product separated from the solution. The mother liquor was syringed off and the product dried under reduced pressure.

For $[Cp(CO)_2Fe(CH_2)_4W(CO)_3Cp]$. The crude product was recrystallised from CH_2Cl_2/hexane.

Preparation of $[Cp^*(CO)_2Fe(CH_2)_nML_y]$*, n = 3–5,* $ML_y = Ru(CO)_2Cp$*; n = 4,* $ML_y = Re(CO)_5$*; n = 3,* $ML_y = Fe(CO)_2Cp$

A solution of the sodium salt of the appropriate transition metal anion (1.06 mmol) in THF (4 ml) was added to a solution of $[Cp^*Fe(CO)_2\{(CH_2)_nI\}]$ (0.77 mmol) in THF (4 ml) at −78 °C with stirring over 5 minutes. The solution was allowed to attain room temperature and stirred until the reaction was judged to be complete by IR monitoring in the ν(CO) region. The solvent was removed under reduced pressure. The product was extracted with hexane, filtered, concentrated and transferred to an alumina column. Elution with hexane gave a yellow band which was collected, concentrated, and cooled to −78 °C. The product separated from the solution. The mother liquor was syringed off and the product dried under reduced pressure.

Acknowledgements

We thank Dr J.M. Steyn of the Department of Pharmacology, University of the Orange Free State, Professor J.C.A. Boeyens of the Chemistry Department, University of the Witwatersrand, and Mr J.D. Malan of Rembrandt International, Stellenbosch for the use of their mass spectrometers. We also thank Mr G. Grierson (Rembrandt) for recording some of the mass spectra, Mr P.A. Makhesha for preparing some iodoalkyl iron complexes, and Mr N. Ahmed for the preparation of $[CpRu(CO)_2]_2$. Finally, we thank the University of Cape Town, the FRD, the Chamber of Mines and SASOL for support.

References

1 R.D. Adams, Polyhedron, 7 (1988) 2251 and following papers.

2 D.A. Roberts and G.L. Geoffroy, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, Vol. 6, 1982, p. 763.

3 A.L. Balch, B.J. Davis, F. Neve and M.M. Olmstead, Organometallics, 8 (1989) 1000 and references therein.

4 P. Braunstein and E. de Jesus, J. Organomet. Chem., 365 (1989) C19.

5 X.L.R. Fontaine, G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1988) 1185.

6 H.A. Jenkins, S.J. Loeb and D.W. Stephen, Inorg. Chem., 28 (1989) 1998.

7 S. Rosenberg, W.S. Mahoney, J.M. Hayes, G.L. Geoffroy and A.L. Rheingold, Organometallics, 5 (1989) 1065.

8 F. Ozawa, J.W. Park, P.B. Mackenzie, W.P. Schaefer, L.M. Henling and R.H. Grubbs, J. Am. Chem. Soc., 111 (1989) 1319.

9 E.N. Jacobsen, K.I. Goldberg and R.G. Bergman, J. Am. Chem. Soc., 110 (1988) 3706.

10 S.J. Davies, J.A.K. Howard, M.U. Pilotti and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1989) 2289 and references therein.

11 B. Olgemoller and W. Beck, Chem. Ber., 114 (1981) 867.

12 K. Raab, U. Nagel and W. Beck, Z. Naturforsch. 38 B, (1983) 1466.

13 J.R. Moss, J. Organomet. Chem., 231 (1982) 229.

14 M. Cooke, N.J. Forrow and S.A.R. Knox, J. Chem. Soc., Dalton Trans., (1983) 2435.

15 H.B. Friedrich, P.A. Makhesha, J.R. Moss and B.K. Williamson, J. Organomet. Chem., 384 (1990) 325.

16 S.J. Archer, K.P. Finch, H.B. Friedrich, J.R. Moss and A.M. Crouch, S. Afr. J. Chem., submitted.

17 H. Adams, N.A. Bailey and M.J. Winter, J. Chem. Soc., Dalton Trans., (1984) 273.

18 L. Pope, P. Sommerville, M. Laing, K.J. Hindson and J.R. Moss, J. Organomet. Chem., 112 (1976) 309.

19 R.B. King, J. Am. Chem. Soc., 90 (1968) 1417.