The synthesis, characterisation and properties of long chain alkyl complexes of the type [CpM(CO)₂R] (Cp = η5-C5H5; M = Fe or Ru; R = n-C6H13 to n-C12H25)

The synthesis, characterisation and properties of long chain alkyl complexes of the type $[CpM(CO)_2R]$ $(Cp = \eta^5\text{-}C_5H_5;\ M = Fe\ or\ Ru;\ R = n\text{-}C_6H_{13}\ to\ n\text{-}C_{12}H_{25})$

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Abstract

The long chain alkyl compounds $[CpM(CO)_2R]$ have been synthesized by the reaction of $Na[CpM(CO)_2]$ with the appropriate n-alkyl chloride or bromide $(Cp = \eta^5\text{-}C_5H_5;\ M = Fe\ or\ Ru;\ R = n\text{-}C_6H_{13}\ to\ n\text{-}C_{12}H_{25})$. The majority of the compounds are new and have been fully characterized by microanalysis, IR, ^1H and ^{13}C NMR and mass spectroscopy. The data are discussed and some properties of the compounds are described.

Introduction

Metal alkyl compounds are the cornerstone of organometallic chemistry and their properties have been studied extensively because of their fundamental importance [1,2]. These compounds are also particularly significant as models for metal alkyl intermediates in a wide variety of important homogeneous and heterogeneous catalytic reactions. These catalytic reactions include the Fischer–Tropsch synthesis as well as the hydrogenation, hydroformylation, isomerisation and polymerisation of alkenes.

The majority of the studies on alkyl compounds, L_nMR, have been carried out on compounds where $R = CH_3$, C_2H_5 or C_3H_7, i.e. short chain alkyl (SCA) compounds. Relatively few studies have been carried out on long chain alkyl (LCA) metal compounds. Studies on SCA transition metal compounds can lead to new information particularly about chain growth processes in catalytic reactions, whereas studies on LCA compounds may have more significance to termination steps. In view of the importance of carbon chain termination steps in catalytic reactions, such as the Fischer–Tropsch reaction where termination to give the gasoline fraction (C_6 to C_{12}) might be desirable or in polymerisation reactions where a specific polymer chain length may be required, it is surprising that so few studies on LCA transition metal compounds have been carried out. This is even more remarkable since it has been clearly shown that some reactions of metal alkyl compounds, which are

fundamental to chemistry and key reactions to catalysis, are dependent on the alkyl chain length, at least up to C_3. Thus for example, the rates of Co–C bond cleavage reactions by iodine in a series of alkylcobaloximes are dependent on the alkyl group [3], so is the rate of CO insertion in $[Mn(CO)_5R]$ [4] and C_2H_4 insertion into Sc–C in $[Cp^*_2ScR]$ [5] and β-hydrogen elimination from $[Cp^*_2ScR]$ [5]. Also, theoretical studies of Berke and Hoffman show how activation parameters for migration of n-alkyl groups in metal alkyl complexes are a function of the chain length of the alkyl group [6].

In the present study we chose the metals Fe and Ru since it is these metals that are active Fischer–Tropsch catalysts and also they are known to form metal alkyl compounds of the type $[CpM(CO)_2R]$.

Experimental

All reactions were carried out under nitrogen using standard Schlenk tube techniques. Tetrahydrofuran (THF) was distilled from sodium before use. The alkyl halides were obtained from the suppliers shown, with % purity in parentheses: n-C_6H_{13}Cl (99%), n-C_7H_{15}Cl (97%), n-C_8H_{17}Cl (99%), n-C_9H_{19}Cl (99%), n-$C_{11}H_{23}$Br (99%) from Aldrich; n-$C_{10}H_{21}$Br (98%) from Merck and n-$C_{12}H_{23}$Br from Sigma. $[CpRu(CO)_2]_2$ was prepared by the method of Knox and Doherty [7] and $[CpFe(CO)_2]_2$ was obtained from Strem.

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. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin–Elmer 983 spectrophotometer. ^1H NMR spectra were recorded either on a Bruker WH90 or a Varian XR 200 spectrometer. ^{13}C NMR spectra were recorded on a Varian XR 200 spectrometer. Low resolution mass spectra were recorded with a VG Micromass 16F spectrometer, operating at 70 eV ionising voltage. The source temperature was raised from room temperature until the spectrum was observed. High resolution mass spectra were recorded on an AEI MS 902 mass spectrometer.

General method for the preparation of [CpFe(CO)$_2$R] (R = n-C$_6$H$_{13}$ to n-C$_{12}$H$_{25}$)

A solution of Na[CpFe(CO)$_2$] (5.6 mmol) in THF (20 ml) was added dropwise over 10 min to the alkyl halide (ca. 4.5 mmol) at 0°C with stirring. The solution was then stirred for a further 2–2½ h at room temperature. The solvent was removed under reduced pressure leaving a brown oily residue. This was extracted with hexane (3 × 40 ml), filtered and the solvent removed under reduced pressure yielding an orange oil with crude yield 90–100%. The oil was transferred to a deactivated alumina column and eluted with hexane. A yellow band was collected and the solvent removed under reduced pressure. The oil was then dried *in vacuo*. If necessary, the sample was dissolved in hexane and filtered before drying.

General method for the preparation of [CpRu(CO)$_2$R] (R = n-C$_6$H$_{13}$ to n-C$_{12}$H$_{25}$)

A solution of Na[CpRu(CO)$_2$] (2 mmol) in THF (11 ml) was added dropwise over 5 min to the alkyl halide (1.7 mmol) at 0°C with stirring. The solution was then stirred for ca. 17 h at room temperature. The solvent was removed under reduced pressure leaving an orange-brown residue. This was extracted with hexane

Table 1

Data for CpM(CO)$_2$R

Compound	M	R	Yield (%)	m.p. (°C)	Elemental analysis [a] (%)	
					C	H
1a	Fe	n-C$_6$H$_{13}$	96	< −12	60.6 (59.6)	7.3 (6.9)
1b	Ru	n-C$_6$H$_{13}$	50	oil	50.8 (51.3)	5.9 (5.9)
2a	Fe	n-C$_7$H$_{15}$	97	< −12	61.4 (60.9)	7.3 (7.3)
2b	Ru	n-C$_7$H$_{15}$	96	oil	52.5 (52.3)	6.3 (6.2)
3a	Fe	n-C$_8$H$_{17}$	84	−4–0	61.5 (62.1)	7.7 (7.7)
3b	Ru	n-C$_8$H$_{17}$	78	oil	52.5 (53.7)	6.1 (6.3)
4a	Fe	n-C$_9$H$_{19}$	76	12–14	62.4 (63.2)	7.7 (8.0)
4b	Ru	n-C$_9$H$_{19}$	65	oil	55.0 (55.6)	6.9 (7.3)
5a	Fe	n-C$_{10}$H$_{21}$	98	6–8	63.8 (64.2)	8.2 (8.3)
5b	Ru	n-C$_{10}$H$_{21}$	75	oil	56.2 (56.2)	7.0 (7.2)
6a	Fe	n-C$_{11}$H$_{23}$	88	27–29	65.1 (65.1)	8.6 (8.4)
6b	Ru	n-C$_{11}$H$_{23}$	90	oil	56.5 (57.3)	7.5 (7.4)
7a	Fe	n-C$_{12}$H$_{25}$	70	22–24	64.9 (65.9)	8.7 (8.7)
7b	Ru	n-C$_{12}$H$_{25}$	43	oil	59.4 (58.3)	7.7 (7.7)

[a] Calculated values in parentheses.

Table 2

^{1}H NMR data for [CpM(CO)$_2$R] [a]

	R	Cp	M–CH$_2$	(CH$_2$)$_x$	CH$_3$
M = Fe	n-C$_6$H$_{13}$	4.65 s	1.38 m	1.21 bs (8 H)	0.81
	n-C$_7$H$_{15}$	4.72 s	1.45 m	1.28 bs (10 H)	0.89
	n-C$_8$H$_{17}$	4.70 s	1.43 m	1.24 bs (12 H)	0.87
	n-C$_9$H$_{19}$	4.70 s	1.44 m	1.25 bs (14 H)	0.87
	n-C$_{10}$H$_{21}$	4.68 s	1.42 m	1.25 bs (16 H)	0.90
	n-C$_{11}$H$_{23}$	4.70 s	1.44 m	1.26 bs (18 H)	0.88
	n-C$_{12}$H$_{25}$	4.68 s	1.43 m	1.25 bs (20 H)	0.88
M = Ru	n-C$_6$H$_{13}$	5.19 s	1.60 m	1.24 bs (8 H)	0.84
	n-C$_7$H$_{15}$	5.18 s	1.58 m	1.20 bs (10 H)	0.82
	n-C$_8$H$_{17}$	5.20 s	1.65 m	1.28 bs (12 H)	0.88
	n-C$_9$H$_{19}$	5.22 s	1.65 m	1.27 bs (14 H)	0.90
	n-C$_{10}$H$_{21}$	5.14 s	1.60 m	1.23 bs (16 H)	0.87
	n-C$_{11}$H$_{23}$	5.22 s	1.61 m	1.26 bs (18 H)	0.88
	n-C$_{12}$H$_{25}$	5.15 s	1.60 m	1.23 bs (20 H)	0.88

[a] Measured in CDCl$_3$ relative to TMS (δ 0.00 ppm); the methyl protons are triplets ($J = 6.5$ Hz); bs = broad singlet.

Table 3

^{13}C NMR of CpFe(CO)$_2$R in CDCl$_3$ relative to TMS

R	Compound	CO	Cp	FeCH$_2$ (α)	C$_2$ (β)	C$_3$ (γ)	C$_4$ (δ)	C$_5$ (ϵ)	C$_6$	C$_7$	C$_8$	C$_9$	C$_{10}$	C$_{11}$	C$_{12}$
n-hexyl	1a	217.73	85.30	3.81	38.31	34.58	31.68	22.77	14.14						
n-heptyl	2a	217.74	85.31	3.82	38.38	34.90	29.14	32.03	22.72	14.13					
n-octyl	3a	217.74	85.23	3.81	38.37	34.93	29.43	29.43	31.96	22.69	14.13				
n-nonyl	4a	217.74	85.21	3.83	38.37	34.94	29.46^a	29.74^a	29.39	31.92	22.70	14.13			
n-decyl	5a	217.73	85.30	3.81	38.37	34.93	29.46^a	29.70^a	29.78^a	29.36	31.93	22.69	14.11		
n-undecyl	6a	217.72	85.29	3.81	38.37	34.93	29.46^a	29.72^a	29.72^a	29.22^a	29.06	31.92	22.70	14.12	
n-dodecyl	7a	217.73	85.29	3.83	38.38	34.94	29.47^a	29.47^a	29.71^a	29.71^a	29.71^a	29.38	31.93	22.70	14.13

^{a} Assignments of these peaks are ambiguous as the peaks are so close together.

Table 4

^{13}C NMR for CpRu(CO)$_2$R in CDCl$_3$ relative to TMS

R	Compound	CO	Cp	RuCH$_2$ (α)	C$_2$ (β)	C$_3$ (γ)	C$_4$ (δ)	C$_5$ (ϵ)	C$_6$	C$_7$	C$_8$	C$_9$	C$_{10}$	C$_{11}$	C$_{12}$
n-hexyl	1b	202.49	88.55	-3.20	39.80	34.53	31.62	22.78	14.16						
n-heptyl	2b	202.49	88.53	-3.22	39.85	34.82	29.04	32.01	22.70	14.11					
n-octyl	3b	202.46	88.51	-3.24	39.82	34.86	29.43	29.32	31.94	22.68	14.10				
n-nonyl	4b	202.45	88.53	-3.22	39.85	34.87	29.38^a	29.75^a	29.38	31.94	22.70	14.12			
n-decyl	5b	202.45	88.53	-3.21	39.85	34.87	29.79^a	29.69^a	29.37^a	29.37	31.94	22.70	14.13		
n-undecyl	6b	202.46	88.51	-3.24	39.83	34.85	29.76^a	29.71^a	29.64^a	29.36^a	29.36	31.91	22.67	14.09	
n-dodecyl	7b	202.50	88.54	-3.24	39.86	34.88	29.77^a	29.67^a	29.70^a	29.70^a	29.67^a	29.37	31.93	22.69	14.13

^{a} Assignments of these peaks are ambiguous as the peaks are so close together.

Table 5

Mass spectral data for CpFe(CO)$_2$R

Possible assignments	Relative peak intensities						
	1a	2a	3a	4a	5a	6a	7a
Parent, M	7	7 [a]	3	6	3	3 [a]	3
$M - CO$	25	20 [a]	22	13	10	9 [a]	8
$M - 2CO$	8		5			3	
$M - 2CO - H$	24		26	25			
$M - 2CO - 2H$	100	100 [a]	100	100	100	100 [a]	
$M - 2CO - 4H$	24	21			25		
$M - 2CO - 6H$	43	38 [a]	44	29	23	23	100
CpFe(CO)H	14	14	17	11	13	12	
CpFeH	29	29	38	19		26	
$M - 2CO - Cp - 3H$	4		16	15		18 [a,b]	
C$_3$H$_7$	33	27	11	15	42	44	14
CpFe(C$_4$H$_7$)	16		11			3	
FeC$_{12}$H$_{19}$							17

[a] Confirmed by high resolution spectroscopy. [b] Peak could correspond to C$_{15}$H$_{12}$O.
All spectra exhibit most of the peaks characteristic of [CpFe(CO)$_2$] species viz. the ions: (m/z) [CpFe(CO)$_2$]$^+$ (177), [CpFe(CO)]$^+$ (149), [CpFe]$^+$ (121), [(C$_3$H$_3$)Fe]$^+$ (95), [Fe]$^+$ (56) and [Cp$_2$Fe]$^+$ (186). Peaks corresponding to the ions [CpFe(CO)(C$_3$H$_x$)]$^+$ ($x = 3,5$) or [CpFe(C$_3$H$_x$)]$^+$ ($x = 7,9$) sometimes appear in the spectra of these alkyl compounds.

(3 × 40 ml), filtered and the solvent removed under reduced pressure yielding an oil with crude yield 90–100%. The oil was transferred to a deactivated alumina column and eluted with hexane. A colourless band was collected, using IR to detect the presence of the product. The solvent was removed under reduced pressure and the oil was dried.

Table 6

Mass spectral data for CpRu(CO)$_2$R

Possible assignments	Relative peak intensities						
	1b	2b	3b	4b	5b	6b	7b
Parent, M	16	10 [a]	17	7	22	6	18
$M - CO$	59	54 [a]	62		40	29	
$M - CO - 2H$				23			50
$M - 2CO - 4H$	100	100 [a]	100	100 [b]	54	76 [b]	95
CpRu(C$_6$H$_7$)	73	19	16	12	12	13 [c]	
C$_3$H$_7$	10	15 [c]	57		100	27	100
RuC$_3$H$_2$	12	17	11		21 [c]		55 [c]
$M - 2CO - Cp - H$				37			
CpRu(CO)$_2$	66	57 [a]	82	57 [c]	65	55 [c]	69
CpRu(CO)	80	58	74	57 [c]	28	41 [c]	48
CpRu	93	80	95	100	24	42 [c]	61
Cp$_2$Ru	12	10	13				
CpRu(CO)$_2$(C$_2$H$_4$)							16

[a] Confirmed by high resolution. [b] Number of hydrogens lost uncertain. [c] Exact position of this peak uncertain.

For the iron and ruthenium compounds, further purification, if necessary, was carried out by recrystallisation from hexane at $-78°C$. Yields and analytical data are given in Table 1, ^{1}H NMR data in Table 2, ^{13}C NMR data in Tables 3 and 4 and mass spectral data in Tables 5 and 6.
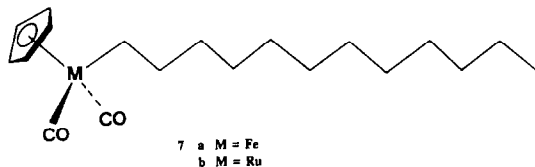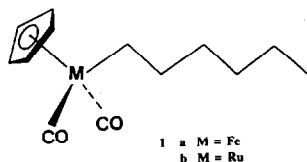
Results

The long chain alkyl compounds were all prepared by the same general route:

$$Na[CpM(CO)_2] + RX \rightarrow [CpM(CO)_2R] + NaX \tag{1}$$

$$(X = Cl \text{ or } Br)$$
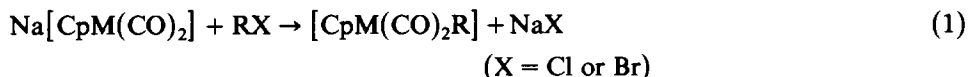
n-R	Fe	Ru
C_6H_{13}	1a	1b
C_7H_{15}	2a	2b
C_8H_{17}	3a	3b
C_9H_{19}	4a	4b
$C_{10}H_{21}$	5a	5b
$C_{11}H_{23}$	6a	6b
$C_{12}H_{25}$	7a	7b

i.e. we have synthesized the homologous series of compounds 1–7.

Previously the SCA compounds of the type $[CpFe(CO)_2R]$ ($R = CH_3$ [8–11], CH_2CH_3 [8,11,12], ^nPr [11–13], ^nBu [9,11,14] and $n-C_5H_{11}$ [15]) have been reported along with some characterisation data; the iron compounds ($R = n-C_6H_{13}$, $n-C_7H_{15}$ or $n-C_8H_{17}$) have only been briefly mentioned [11,13]. Some studies on the SCA ruthenium compounds, $[CpRu(CO)_2R]$ ($R = CH_3$, CH_2CH_3 or ^nBu) have been reported [15–18].

In the syntheses (eq. 1), an excess of $Na[CpM(CO)_2]$ was used to ensure that no alkyl halide remained at the end of the reaction because of difficulty in separating this from the metal alkyl products. In this way, the pure LCA metal compounds could be obtained in high yield. The iron complexes (1a–7a) are yellow-brown oils or low-melting yellow crystalline solids which are stable in air for short periods. Under a nitrogen atmosphere and in the dark, they can be kept for several months at $-15°C$ without appreciable decomposition. The LCA iron compounds decom-

pose more slowly than their short chain analogues, such as $[CpFe(CO)_2(n-C_3H_7)]$, under similar conditions. The ruthenium compounds (**1b–7b**) are even more stable than their iron analogues under all conditions. Thus, even though the compounds **1–7** have β-hydrogens, they show no predilection to decompose by β-hydrogen elimination. We will report further details of the decompositions of the compounds $[CpM(CO)_2R]$ in a later paper [19].

All the new compounds **1–7** were fully characterized by m.p., microanalysis (Table 1), IR, ^1H NMR (Table 2), ^{13}C NMR (Tables 3 and 4) and mass spectrometry (Tables 5 and 6).

IR spectra

All the compounds **1–7** show two strong $\nu(CO)$ bands in their IR spectra in hexane solution. For the iron compounds these bands appear at 2008 and 1954 cm^{-1}, whereas for the ruthenium compounds they appear at 2018 and 1959 cm^{-1}, suggesting that the C–O bond in the iron compounds is weaker than the C–O bond in the ruthenium analogues; conversely, the Fe–CO bond may be stronger than the Ru–CO bond. There is no significant change in $\nu(CO)$ on changing the length of the alkyl chain.

NMR spectra

Separate resonances were observed for the Cp and methyl protons of the alkyl group; these showed no variation with alkyl chain length.

The methylene protons appear as a broad singlet. Thus, the integration is the only way to distinguish between say **1a** and **3a** using ^1H NMR. The chemical shifts of Cp bound to iron are lower (δ 4.68) than for Cp bound to ruthenium (δ 5.15) as has been found previously in related compounds [20].

The ^{13}C NMR data for the iron alkyl compounds (**1a–7a**) are given in Table 3 while that for the ruthenium alkyl compounds (**1b–7b**) are in Table 4. Assignments were made by comparison with data reported for related compounds in particular the binuclear compounds $[Cp(CO)_2Fe(CH_2)_nML_y]$ [20] and $[Cp(CO)_2Fe(CH_2)_nRu-(CO)_2Cp]$ [21] as well as with the compounds $[CpFe(CO)_2\{(CH_2)_nX\}]$ [22], $[CpRu(CO)_2\{(CH_2)_nX\}]$ (X = Br or I) [23] and $CH_3(CH_2)_nX$ [24]. The Cp and CO resonances are dependent on the metal, they appear at expected positions and are independent of the alkyl chain length. For compounds **1–3**, all the carbon atoms of the alkyl chains could be assigned. For compounds **4–7**, the chemical shifts of the central carbon atoms are very close together and the assignments are not unambiguous, as is found for substituted n-alkanes, $CH_3(CH_2)_nX$ [24]. Effects of the metal are only evident on the first two carbon atoms of the alkyl chain.
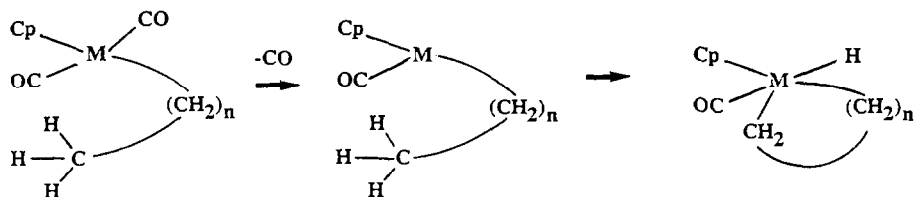
Mass spectra

All the alkyl compounds **1–7** showed parent molecular ions in their mass spectra. The main fragmentation pathways begin as follows: (1) M, $M - CO$, $M - 2CO - 2H$; (2) M, $M - R$, $M - R - CO$, $M - R - 2CO$.

Other peaks are also observed which are characteristic of $[CpM(CO)_2Y]$ compounds [20]. For pathway 1, the loss of (2CO and 2H) was confirmed by high resolution measurements (see Tables 5 and 6).

This loss of (2CO and 2H) from $[CpFe(CO)_2R]$ has been observed before for other iron alkyl compounds [25]. We believe that this and further loss of up to 6H

may be a result of "remote functionalization" [26] where the C–H bond of the methyl group of the alkyl chain is activated by the coordinatively unsaturated metal atom to give a metallacycle after the initial loss of CO.


Further loss of hydrogen can then occur by β-hydrogen elimination, without loss of the alkyl residue. Support for the proposal that it is a methyl hydrogen that is initially added to the iron comes from the mass spectra of the compounds [CpFe(CO)$_2${(CH$_2$)$_n$X}] (n = 3–10; X = Br or I) which show different fragmentation behaviour [22] to that shown by their alkyl analogues. Experiments are underway to test this remote functionalisation proposal [19].

Discussion

We report the synthesis and characterisation of the alkyl compounds of type [CpM(CO)$_2$R] (M = Fe or Ru; R = n-C$_6$H$_{13}$ to n-C$_{12}$H$_{25}$). These compounds make up one of the first known series of long chain alkyl compounds. Even though these compounds have β-hydrogens, they are moderately stable to heat, light and air, particularly the ruthenium compounds. For iron, the LCA compounds described in this paper appear more stable than their lighter homologues under identical conditions.

The compounds 1–7 can be models for alkyl intermediates in catalytic reactions such as the Fischer–Tropsch reaction. In particular, the ruthenium compounds **1b–7b** may be close models for alkyl ruthenium intermediates of the type "Ru(CO)$_x$(hydrocarbon chain)" postulated by Pichler and co-workers in the ruthenium catalyzed synthesis of polymethylene from CO and hydrogen [27,28]. Alkyl ruthenium species were actually isolated by Pichler at the end of a catalytic run with a ruthenium catalyst and using a CO, H$_2$ pressure of 1000 atm and a temperature of about 120°C. The brown ruthenium containing oils were partially characterized as Ru(CO)$_x$(CH$_2$R) by IR, ^{1}H NMR and elemental analysis. Subsequently, these alkyl ruthenium intermediates have been variously referred to as CH$_3$(CH$_2$)$_n$Ru(CO)$_x$ [29] or (polymer chain)Ru(CO)$_x$ [30], however, they are considered to be crucial intermediates in the polymethylene synthesis [27–30]. Pichler's alkyl ruthenium species show two ν(CO) bands of equal intensity in the IR spectra at 2049 and 1980 cm^{-1}. This compares with compounds [CpRu(CO)$_2$R] **(1b–7b)** which also show two ν(CO) bands of equal intensity but at 2018 and 1959 cm^{-1}. This suggests to us that in Pichler's compounds, x may be 2 and that the oxidation state of the Ru may be greater than 2. In the apparent absence of any ν(Ru = O) in Pichler's IR spectra, we tentatively suggest that a more accurate formulation of Pichler's alkyl ruthenium species may be:
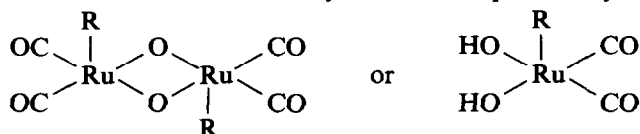
Since ruthenium is the most active and selective catalyst for polymethylene synthesis from CO and hydrogen [31] and since iron is the currently used catalyst in the only commercial CO hydrogenation operation viz. the SASOL plants in South Africa [32], we are continuing our studies on these alkyl iron and ruthenium complexes of type $[CpM(CO)_2R]$.

In a later paper, we will describe further properties of these and related compounds as well as decomposition pathways and their chemical reactivity [19].

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