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Journal of Organometallic Chemistry 564 (1998) 267–276

Journal of Organo metallic Chemistry

# Synthesis, characterization and chemistry of some long chain alkoxycarbonyl manganese pentacarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$ (where $R = n\text{-}C_7H_{15}$ to $n\text{-}C_{10}H_{21}$, $n\text{-}C_{12}H_{25}$, $n\text{-}C_{14}H_{29}$, and $n\text{-}C_{16}H_{33}$)

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Accepted 27 April 1998

## Abstract

The long chain alkoxycarbonyl complexes, $[Mn(CO)_5\{C(O)OR\}]$, where $R = CH_2R'$, and $R = n\text{-}C_7H_{15}$ to $n\text{-}C_{10}H_{21}$, $n\text{-}C_{12}H_{25}$ and $n\text{-}C_{16}H_{33}$, have been synthesized by the reactions of the acyl complexes $[Mn(CO)_5\{C(O)R'\}]$, where $R' = n\text{-}C_6H_{13}$ to $n\text{-}C_9H_{19}$, $n\text{-}C_{11}H_{23}$ and $n\text{-}C_{15}H_{31}$, with synthesis gas in hexane. In addition, the complexes $[Mn(CO)_5\{C(O)OR\}]$ ($R = n\text{-}C_9H_{19}$ and $n\text{-}C_{14}H_{29}$) have been synthesized by the reactions of the alkyl complexes $[Mn(CO)_5R'']$, where $R'' = n\text{-}C_8H_{17}$ and $n\text{-}C_{13}H_{27}$, with synthesis gas in hexane. These new alkoxycarbonyl complexes have been fully characterized by elemental analysis, melting point, IR, $^1H$-NMR, $^{13}C$-NMR and mass spectroscopy. The thermal behaviour of these complexes has been investigated by differential scanning calorimetry and thermal gravimetry analysis. The reaction of the acyl complex $[Mn(CO)_5\{C(O)C_{11}H_{23}\}]$ with synthesis gas in THF gave $[Mn_2(CO)_{10}]$ (95%) and the alcohol $n\text{-}C_{12}H_{25}OH$ (92%). The reaction of the alkoxycarbonyl complex $[Mn(CO)_5\{C(O)OC_{12}H_{25}\}]$ with synthesis gas in hexane at 85°C gave the formate $HCO_2C_{12}H_{25}$ (66%), the alcohol $n\text{-}C_{12}H_{25}OH$ (33%) and $[Mn_2(CO)_{10}]$ (96%). The same reaction as above in THF yielded the formate $HCO_2C_{12}H_{25}$ (12%), the alcohol $n\text{-}C_{12}H_{25}OH$ (46%) and the ester $CH_3(CH_2)_3CO_2C_{12}H_{25}$ (43%) as well as $[Mn_2(CO)_{10}]$ (63%). These studies show that the reactions of the acyl complexes $[Mn(CO)_5\{C(O)R'\}]$, the alkyl complexes $[Mn(CO)_5R'']$ and the alkoxycarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$ with synthesis gas are both solvent and temperature dependent.

*Keywords:* Manganese; Alkoxycarbonyl; Acyl; Alkyl; Alcohol

## 1. Introduction

The study of transition metal alkoxycarbonyl complexes $[L_nM\{C(O)OR\}]$ is of general interest, because these complexes have been recognized as intermediates and/or products in a number of important heterogeneous and homogeneous catalytic processes [1–10], such as hydroformylation and hydrocarboxylation of olefins [1–5], carbonylation of alcohols and alkyl halides [1,6–10], Fischer–Tropsch synthesis [2], synthesis of alkyl carbonates and of oxalate esters [8].

Investigations of the synthesis and chemistry of the alkyl complexes $[Mn(CO)_5R'']$ and acyl complexes $[Mn(CO)_5\{C(O)R'\}]$ have been extensively carried out in this laboratory [11–14]. During our studies on the reactions of such alkyl and acyl complexes with synthesis gas (syngas, $CO/H_2$), we found that the reaction products are largely solvent dependent. Long chain alkoxycarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$ or alcohols can be selectively obtained from the reaction of

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*PII* S0022-328X(98)00644-5

[Mn(CO)$_5$R″] (or [Mn(CO)$_5${C(O)R′}]) with CO/H$_2$, when the solvent is hexane or THF. Some short chain alkoxycarbonyl complexes [Mn(CO)$_5${C(O)OR}] (R = $C_2H_5$, $n$-$C_6H_{13}$) have been previously reported in the literature [15–17].

We now report our studies (1) on the synthesis of long chain alkoxycarbonyl complexes [Mn(CO)$_5${C(O)-OR}] (R = CH$_2$R′) by the reaction of the acyl complexes [Mn(CO)$_5${C(O)R′}] (R′ = $n$-$C_6H_{13}$ to $n$-$C_9H_{19}$, $n$-$C_{11}H_{23}$, and $n$-$C_{15}H_{31}$) with syngas, or by the reaction of the alkyl complexes [Mn(CO)$_5$R″] (R″ = $n$-$C_8H_{17}$ and $n$-$C_{13}H_{27}$) with syngas in hexane; (2) on some reactions of the alkoxycarbonyl complexes [Mn(CO)$_5$-{C(O)OR}].

## 2. Results and discussion

### 2.1. Synthesis and characterization of alkoxycarbonyl complexes [Mn(CO)$_5${C(O)OR}]

### 2.1.1. Synthesis

The acyl complexes [Mn(CO)$_5${C(O)R′}] (where R′ = $n$-$C_6H_{13}$ to $n$-$C_9H_{19}$, $n$-$C_{11}H_{23}$, and $n$-$C_{15}H_{31}$) and the alkyl complexes [Mn(CO)$_5$R″] (R″ = $n$-$C_8H_{17}$ and $n$-$C_{13}H_{27}$) were synthesized according to the methods reported by Andersen and Moss [11]. The long chain alkoxycarbonyl complexes [Mn(CO)$_5${C(O)OR}] (R = $n$-$C_7H_{15}$, **1**; $n$-$C_8H_{17}$, **2**; $n$-$C_9H_{19}$, **3**; $n$-$C_{10}H_{21}$, **4**; $n$-$C_{12}H_{25}$, **5**; and $n$-$C_{16}H_{33}$, **7**) were synthesized by the reaction of the corresponding acyl complexes [Mn(CO)$_5${C(O)R′}] with syngas in hexane as shown in Scheme 1. This method is similar to that reported by Orchin and co-workers [16,17] for the preparation of [Mn(CO)$_5${C(O)OR}] (R = $C_2H_5$ and $n$-$C_6H_{13}$).

Alternatively, the alkoxycarbonyl complexes [Mn(CO)$_5${C(O)OR}] (R = $n$-$C_9H_{19}$, **3**, $n$-$C_{14}H_{29}$, **6**) can be synthesized by the reaction of the alkyl complexes [Mn(CO)$_5$R″] (R″ = $n$-$C_8H_{17}$ and $n$-$C_{13}H_{27}$) with syngas in hexane. This is to be expected since compounds of the type [Mn(CO)$_5$R″] are known to react with CO to give [Mn(CO)$_5${C(O)R″}] under mild conditions [11,14] (Scheme 2).

$$[\mathrm{Mn(CO)_5\{C(O)R'\}}] + \mathrm{CO/H_2} \xrightarrow{\text{hexane}} [\mathrm{Mn(CO)_5\{C(O)OR\}}]$$

| **n-R′** | **n-R** | **Compd. no. of alkoxycarbonyl product** |
|---|---|---|
| $C_6H_{13}$ | $C_7H_{15}$ | **1** |
| $C_7H_{15}$ | $C_8H_{17}$ | **2** |
| $C_8H_{17}$ | $C_9H_{19}$ | **3** |
| $C_9H_{19}$ | $C_{10}H_{21}$ | **4** |
| $C_{11}H_{23}$ | $C_{12}H_{25}$ | **5** |
| $C_{15}H_{31}$ | $C_{16}H_{33}$ | **7** |

Scheme 1.

$$[\mathrm{Mn(CO)_5R''}] + \mathrm{CO/H_2} \xrightarrow{\text{hexane}} [\mathrm{Mn(CO)_5\{C(O)OR\}}]$$

| **n-R″** | **n-R** | **Compd. no. of alkoxycarbonyl product** |
|---|---|---|
| $C_8H_{17}$ | $C_9H_{19}$ | **3** |
| $C_{13}H_{27}$ | $C_{14}H_{29}$ | **6** |

Scheme 2.

The new complexes **1**–**7** were obtained as low-melting white or off-white crystalline solids. These complexes have been fully characterized by melting point, elemental analysis (Table 1), IR (Table 2), $^1$H-NMR (Table 3), and $^{13}$C-NMR (Table 4), and mass spectroscopy (Tables 1 and 5).

### 2.1.2. Characterization

The IR spectral data of the complexes **1**–**7** are in good agreement with the values reported for other related [Mn(CO)$_5${C(O)OR}] complexes [15–17] and show peaks (Table 2) in hexane solution at ca. 2124w, ($A_1$); 2031s, (E); 2007s cm$^{-1}$, ($A_1$); for $\nu$(CO) terminal carbonyls; and at about 1652m and 1021m cm$^{-1}$ for $\nu$(C=O) acyl and $\nu$(C–O–C), respectively. There is no significant variation in the $\nu$(CO) upon changing the length of the alkyl chain.

The $^1$H-NMR data for the complexes **1**–**7** reported in Table 3 are in good agreement with the data reported for complexes of the type [Mn(CO)$_5${C(O)OR}] [15–17]. From the $^1$H-NMR data, it can be seen that separate resonances are observed for the $\alpha$ [$\alpha$ to C(O)O, etc.] and $\beta$ protons and the methyl protons of the alkyl chain. These resonances are not affected by the alkyl chain length. Thus integration is the only way to distinguish these complexes by $^1$H-NMR spectroscopy. The resonances of the $\alpha$ and $\beta$ protons of the alkyl chain in these alkoxycarbonyl complexes shift downfield compared with the $\alpha$ and $\beta$ protons in the starting acyl complexes [11], due to the deshielding effect of the electron-withdrawing C(O)O group.

No $^{13}$C-NMR data have been previously reported for the alkoxycarbonyl complexes [Mn(CO)$_5${C(O)OR}] [15–17]. We have recorded the $^{13}$C-NMR spectra for these complexes (except **6**) and the data are presented in Table 4, with suggested assignments. The assignments were made by comparison with the related acyl com-

Table 1
Data for the alkoxycarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$

| Compound no. | *n*-R | M[a] calc. | $M^{+}$[b] observed | Yield (%) | M.p. (°C) | Elemental analysis (%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | C found (calc.) | H found (calc.) |
| **1** | $C_7H_{15}$ | 338 | 338 | 40 | 51-53 | 46.25 (46.15) | 4.46 (4.44) |
| **2** | $C_8H_{17}$ | 352 | 352 | 44 | 52-54 | 47.31 (47.73) | 4.78 (4.83) |
| **3** | $C_9H_{19}$ | 366 | 366 | 47 | 49-51 | 48.86 (49.18) | 5.06 (5.19) |
| **4** | $C_{10}H_{21}$ | 380 | 380 | 45 | 48-51 | 50.23 (50.53) | 5.60 (5.53) |
| **5** | $C_{12}H_{25}$ | 408 | 408 | 87 | 54-55 | 53.69 (52.95) | 6.42 (6.17) |
| **6** | $C_{14}H_{29}$ | 436 | 436 | 32 | 35-37 | c | c |
| **7** | $C_{16}H_{33}$ | 464 | 464 | 44 | 49-52 | c | |

[a] M is the calculated molecular mass.

[b] $M^+$ is the molecular ion observed in the mass spectrum of the compound.

[c] No satisfactory data were obtained.

plexes $[Mn(CO)_5\{C(O)R'\}]$ [11] and by means of a heteronuclear correlation (HETCOR) experiment. For all the complexes, the spectra show the terminal carbonyl resonance at $\delta$ 208 ppm and the alkoxycarbonyl carbon (C=O) resonance at $\delta$ 200 ppm in $CDCl_3$ solution. In $C_6D_6$ solution, the resonances of the terminal carbonyl and the alkoxycarbonyl carbon atoms are found at $\delta$ 208 and 198 ppm, respectively. These do not show any variation in chemical shifts with increase in the length of the alkyl chain. The resonances due to the central methylene carbon atoms were not completely resolved and could not be assigned unambiguously, as was observed for the long chain acyl complexes [11].

The low resolution electron impact mass spectra for the complexes **1**–**7** were recorded. Molecular ions are observed for all the compounds under discussion, but are of low intensity. The intensities of the major organometallic peaks of the complexes **5** and **7** are reported in Table 5 with suggested assignments.

Table 2
IR spectroscopic data for the alkoxycarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$ in hexane

| Compound no. | *n*-R | IR ($cm^{-1}$) | | |
|---|---|---|---|---|
| | | $\nu\equiv$(CO) | $\nu$(C=O) | $\nu$(C–O–C) |
| **1** | $C_7H_{15}$ | 2124w, 2031s, 2007s | 1652m | 1022m |
| **2** | $C_8H_{17}$ | 2124w, 2031s, 2007s | 1652m | 1022m |
| **3** | $C_9H_{19}$ | 2124w, 2031s, 2008s | 1651m | 1020m |
| **4** | $C_{10}H_{21}$ | 2124w, 2031s, 2007s | 1652m | 1022m |
| **5** | $C_{12}H_{25}$ | 2126w, 2033s, 2010s | 1654m | 1021m |
| **6** | $C_{14}H_{29}$ | 2126w, 2029s, 2010s | 1657m | 1022m |
| **7** | $C_{16}H_{33}$ | 2125w, 2031s, 2008s | 1654m | 1024m |

W, weak; s, strong; m, medium.

All the complexes show similar fragmentation pathways. The fragmentation pathways for the complex **5** are shown in Scheme 3. The predominant fragmentation pathway is sequential loss of carbonyl groups from the molecular ion, followed by the loss of the OR group. The spectra of these complexes exhibit peaks corresponding to the ions $[Mn(CO)_6]^+$ (*m*/*z* 223), $[Mn(CO)_5]^+$ (*m*/*z* 195), $[Mn(CO)_4]^+$ (*m*/*z* 167), $[Mn(CO)_3]^+$ (*m*/*z* 139), $[Mn(CO)_2]^+$ (*m*/*z* 111), $[Mn(CO)]^+$ (*m*/*z* 83), $[Mn]^+$ (*m*/*z* 55), $[CO_2]^+$ (*m*/*z* 44) and $[CO]^+$ (*m*/*z* 28).

### 2.1.3. Thermal properties of the alkoxycarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$

The thermal behaviour of the complexes **1**–**4** and **7** was studied by DSC. The results are summarized in Table 6. A sharp endothermic peak is seen for each complex in the temperature range which corresponds to the melting range measured by conventional means (Kofler hot-stage microscope). A slight increase of the melting point ($T_{max}$) with the increase of alkyl chain length from $n = 8$ to 10 was observed. Another broad endothermic peak is observed in the DSC traces in the temperature range 103–140°C, all with a maximum at 121–123°C, which corresponds to the decomposition of the complexes. This is supported by the observation of a significant mass loss in the TGA traces of these complexes over the temperature range 80–140°C. The mass remaining after heating these complexes to 200°C corresponds to the degradation of the alkoxycarbonyl complexes to $MnO_2$.

Table 3
$^1$H-NMR data for the alkoxycarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$ (400 MHz, $CDCl_3$)

| Compound no. | *n*-R | $C(O)OCH_2$<br>$^3J(HH)$ | $C(O)OCH_2CH_2$<br>$^3J(HH)$ | $C(O)OCH_2CH_2(CH_2)_n$ | $CH_3$<br>$^3J(HH)$ |
|---|---|---|---|---|---|
| **1** | $C_7H_{15}$ | 4.03, 2H, br | 1.59, 2H, br | 1.27, 8H, br | 0.87, 3H, br |
| **2**[a] | $C_8H_{17}$ | 4.05, 2H, t, 6.4 Hz | 1.59, 2H, qn, 6.1 Hz | 1.27, 10H, br | 0.87, 3H, t, 6.6 Hz |
| **3** | $C_9H_{19}$ | 4.04, 2H, br | 1.59, 2H, br | 1.26, 12H, br | 0.87, 3H, br |
| **4** | $C_{10}H_{21}$ | 4.04, 2H, br | 1.58, 2H, br | 1.26, 14H, br | 0.87, 3H, br |
| **5** | $C_{12}H_{25}$ | 4.03, 2H, br | 1.58, 2H, br | 1.25, 18H, br | 0.87, 3H, br |
| **6** | $C_{14}H_{29}$ | 4.04, 2H, t, 6.4 Hz | 1.58, 2H, br | 1.26, 22H, br | 0.87, 3H, t, 6.8 Hz |
| **7** | $C_{16}H_{33}$ | 4.04, 2H, br | 1.58, 2H, br | 1.25, 26H, br | 0.87, 3H, br |

Br, broad; t, triplet; qn, quintet.

[a] The $^1$H-NMR spectrum for this compound was recorded at 200 MHz in $CDCl_3$.

## 2.2. Reactivity of acyl complexes $[Mn(CO)_5\{C(O)R'\}]$, alkyl complexes $[Mn(CO)_5R'']$ and alkoxycarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$

### 2.2.1. Reactions of the acyl complex $[Mn(CO)_5\{C(O)C_{11}H_{23}\}]$ and the alkyl complex $[Mn(CO)_5(C_9H_{19})]$ with syngas in THF: synthesis of alcohols

We have shown that the reactions of alkyl complexes $[Mn(CO)_5R'']$ or acyl complexes $[Mn(CO)_5\{C(O)R'\}]$ with syngas in hexane give the alkoxycarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$ ($R = CH_2R'$ or $CH_2R''$) as the sole products. Similar results have also been obtained by Orchin and co-workers [16,17]. However, the reactions of the acyl complexes $[Mn(CO)_5\{C(O)R'\}]$ with syngas in the highly polar solvent sulfane were reported to give exclusively aldehydes [17,18].

We have carried out the reactions of the acyl complex $[Mn(CO)_5\{C(O)C_{11}H_{23}\}]$ and the alkyl complex $[Mn(CO)_5(C_9H_{19})]$, respectively, with syngas in THF and found that these reactions give exclusively alcohols and $[Mn_2(CO)_{10}]$ (Schemes 4 and 5). These products were isolated by chromatography on a short silica gel column and identified by their melting points, IR, $^1$H-NMR, $^{13}$C-NMR and mass spectroscopy. No aldehyde, formate, or the alkoxycarbonyl complex was detected for these reactions.

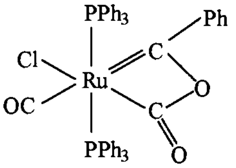
The formation of alcohol from the reaction of $[Mn(CO)_5\{C(O)C_{11}H_{23}\}]$ with syngas in THF has provided further evidence for the previous proposal that the acyl complexes $[Mn(CO)_5\{C(O)R'\}]$ ($R' = R''$) are the most probable intermediates in the reactions of $[Mn(CO)_5R'']$ with syngas [14,20], since the reaction of $[Mn(CO)_5R'']$ with CO is known to give $[Mn(CO)_5\{C(O)R'\}]$ ($R' = R''$) [11,14,21].

Since different products were obtained by the reactions of acyl complexes $[Mn(CO)_5\{C(O)R'\}]$ with syngas in different solvents, this suggests that the solvents play a crucial role in these reactions. The effect of the solvents could be rationalized as follows: (1) in the polar, coordinating solvents, such as in THF, $[HMn(CO)_5]$ could be formed under the reaction conditions, and this hydride might be able to protonate the acyl complex to give a hydroxycarbene species, which can then undergo reaction with $H_2$, as shown in step (a) of Scheme 6. The formation of hydroxycarbene species by protonolysis of acyl complexes has been demonstrated [21,22] and the crystal structure of a cationic hydroxycarbene (shown below)

$[CH_3\_C{=}Mn(CO)_3(DPPP)]^+CF_3SO_3^-$

(DPPP = bis(diphenylphosphino)propane)

has been determined [22]. (2) In non-polar solvents, such as in hexane, the reaction might take place via another route, as shown in step (b) of the Scheme 6, to produce the alkoxycarbonyl species. The ruthenium complex (see below) containing a four-membered metallacycle similar to that of the key intermediate **A** in Scheme 6 has recently been reported [23].



Orchin and co-workers have proposed another mechanism for the formation of $[Mn(CO)_5\{C(O)OR\}]$, and suggested that the insertion of CO into the Mn–OR bond of intermediates $[Mn(CO)_5(OR)]$ might be the key step for the formation of $[Mn(CO)_5\{C(O)OR\}]$ [16,17].

### 2.2.2. Reactivity of the alkoxycarbonyl complexes $[Mn(CO)_5\{C(O)OR\}]$

The reaction of the short chain complex $[Mn(CO)_5\{C(O)OC_2H_5\}]$ with acids was reported to give cationic carbonyls $[Mn(CO)_6]^+$(and $C_2H_5OH$ as the organic product) [24,25]. It was also reported [26] that the reactions of $[Mn(CO)_5\{C(O)OC_2H_5\}]$ with $[HCo(CO)_4]$ or $[HMn(CO)_5]$ give ethyl formate and $[MnCo(CO)_9]$, or ethyl formate and $[Mn_2(CO)_{10}]$, respectively. The reactivity of long chain $[Mn(CO)_5\{C(O)OR\}]$ complexes, especially the reactiv-

Table 4
$^{13}$C-NMR chemical shift ($\delta$ ppm) data for the alkoxycarbonyl complexes [Mn(CO)5{C(O)OR}] (100 MHz, CDCl$_3$)

| Compound no. | $n$-R | CO | C(O)O | OCH$_2$ | OCH$_2$$C$H$_2^a$ | OCH$_2$CH$_2$($C$H$_2$)$_n^b$ | $C$H$_2$CH$_2$CH$_3$ | $C$H$_2$CH$_3$ | CH$_3$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | C$_7$H$_{15}$ | 207.84 | 200.30 | 64.54 | 31.75 | 29.08, 28.88 | 26.07 | 22.54 | 14.03 |
| **2**[c] | C$_8$H$_{17}$ | 207.90 | 200.31 | 64.54 | 31.75 | 29.18, 29.09 | 26.11 | 22.61 | 14.01 |
| **3** | C$_9$H$_{19}$ | 207.83 | 200.31 | 64.55 | 31.85 | 29.50, 29.20, 29.09 | 26.11 | 22.65 | 14.07 |
| **3**[d] | C$_9$H$_{19}$ | 208.45 | 197.81 | 64.70 | 29.58 | 32.23, 29.91 | 26.45 | 23.06 | 14.31 |
| **4** | C$_{10}$H$_{21}$ | 207.97 | e | 64.56 | 31.88 | 29.50, 29.29, 29.23, 29.09 | 26.12 | 22.66 | 14.08 |
| **5** | C$_{12}$H$_{25}$ | 207.82 | 200.32 | 64.57 | 31.92 | 29.64, 29.56, 29.35, 29.25, 29.10 | 26.13 | 22.69 | 14.11 |
| **7** | C$_{16}$H$_{33}$ | 207.86 | 200.33 | 64.57 | 31.92 | 29.68, 29.56, 29.35, 29.25, 29.10 | 26.13 | 22.68 | 14.10 |

[a] The resonance for this carbon atom was assigned tentatively.
[b] Peaks for these carbon atoms were not completely resolved or assigned.
[c] The $^{13}$C-NMR spectrum for this compound was measured at 50 MHz.
[d] C$_6$D$_6$, the assignments were confirmed by a HETCOR experiment.
[e] This peak was not observed.

ity of these complexes under conditions similar to hydroformylation conditions, is unknown. We now report the reactions of [Mn(CO)$_5${C(O)OR}] complexes with syngas in hexane and in THF.

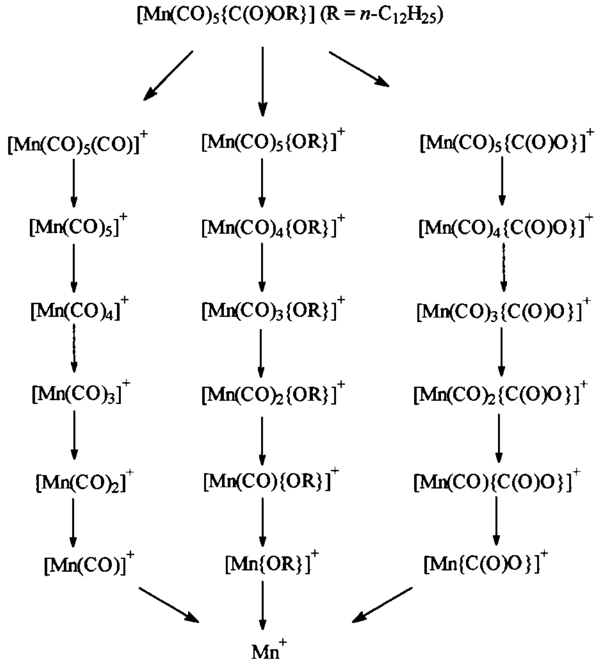
*2.2.2.1. Reaction of [Mn(CO)$_5${C(O)OC$_{12}$H$_{25}$}], **5** with syngas in hexane.* The reaction of **5** with CO/H$_2$ (48 bar) in hexane was carried out at 85°C for 11 h, and gave [Mn$_2$(CO)$_{10}$] quantitatively. The organic products isolated by chromatography were dodecyl formate HCO$_2$C$_{12}$H$_{25}$ in 33% yield, and dodecyl alcohol $n$-C$_{12}$H$_{25}$OH in 66% yield. The identification of these organic products was made by IR, $^1$H and $^{13}$C-NMR, and mass spectroscopy (Scheme 7).

Table 5
Mass spectral data for [Mn(CO)$_5${C(O)OR}]

| Ion[a] | Relative intensities[b] (%) | |
|---|---|---|
| | R = $n$-C$_{12}$H$_{25}$, **5** | R = $n$-C$_{16}$H$_{33}$, **7** |
| M | 0.3 | 0.4 |
| M–CO | 3 | 2 |
| M–4CO | 0 | 0.2 |
| M–5CO | 2 | 1 |
| M–6CO | 100 | 100 |
| M–R | 0.5 | 0.7 |
| M–R–CO | 1 | 0.2 |
| M–R–2CO | 0.3 | 0.3 |
| M–R–3CO | 0.4 | 0.4 |
| M–R–4CO | 0.4 | 0.9 |
| M–R–5CO | 0.5 | 1 |
| M–OR | 21 | 20 |
| M–OR–CO | 6 | 7 |
| M–OR–2CO | 4 | 3 |
| M–OR–3CO | 4 | 4 |
| M–OR–4CO | 5 | 6 |
| M–OR–5CO | 7 | 10 |
| M–OR–6CO (=Mn) | 26 | 27 |

[a] M = [Mn(CO)$_5${C(O)OR}]; all ions have a single positive charge; ion refers to probable assignment.
[b] Peak intensities are relative to [M–6CO], i.e. [MnOR].

The formation of the formate HCO$_2$C$_{12}$H$_{25}$ by the reaction of the alkoxycarbonyl complex **5** with syngas under hydroformylation conditions is not unexpected. In fact, formates have been reported as by-products in the Fischer–Tropsch synthesis [2,27], and alkoxycarbonyl complexes have been suggested as intermediates for the formate formation [1]. Hence, the manganese complexes may serve as model complexes for intermediates involved in the Fischer–Tropsch synthesis. The production of methyl formate by the reaction of CO$_2$, H$_2$ and MeOH might also involve alkoxycarbonyl intermediates [28].



Scheme 3.

Table 6
Thermal analysis data for the complexes [Mn(CO)$_5${C(O)OR}]

| Compound no. | *n*-R | M.p. (°C)[a] | $T_i$ (°C)[b] | $T_{max}$ (°C)[c] | $\Delta H_{endo}$ (kJ mol$^{-1}$)[d] |
|---|---|---|---|---|---|
| **1** | $C_7H_{15}$ | 51–53 | 54.8 | 56.4 | 24.46 |
| **2** | $C_8H_{17}$ | 52–54 | 52.7 | 54.5 | 21.72 |
| **3** | $C_9H_{19}$ | 49–51 | 53.2 | 55.5 | 28.77 |
| **4** | $C_{10}H_{21}$ | 48–51 | 53.5 | 58.0 | 27.46 |
| **7** | $C_{16}H_{33}$ | 49–52 | 54.1 | 56.6 | 32.75 |

[a] Determined on a Kofler hot-stage microscope.

[b] Temperature corresponding to the onset of a peak.

[c] Temperature corresponding to the peak maximum.

[d] Calculated by Perkin Elmer PC Series DSC7 machine (J g$^{-1}$).

*2.2.2.2. Reaction of [Mn(CO)$_5${C(O)OC$_{12}$H$_{25}$}],* ***5*** *with syngas in THF.* Since solvents play a crucial role in product formation, we have also investigated the reaction of **5** with syngas in THF. The reaction was carried out at 60°C for 23 h under a pressure of 48 bar of CO/H$_2$. Chromatographic separation yielded [Mn$_2$(CO)$_{10}$] in 63% yield. The hydride [HMn(CO)$_5$] was detected by IR spectroscopy but this complex was not isolated owing to its instability. The organic products obtained by column chromatography were the alcohol *n*-$C_{12}H_{25}OH$ in 46% yield and the formate $HCO_2C_{12}H_{25}$ in 12% yield. Similar products were obtained for the reaction in hexane. In addition, another product was obtained in 43% yield. This product was identified as the ester $CH_3(CH_2)_3CO_2(CH_2)_{11}CH_3$, on the basis of its mass spectrum ([M]$^+$, 271), IR, $^1$H and $^{13}$C-NMR.

The isolation of the ester product from the reaction of **5** with syngas in THF strongly implied that the solvent THF reacted with **5** under these conditions. Our results show that the solvent indeed plays a crucial role in determining the nature of the products obtained from the reaction of alkoxycarbonyl complexes with syngas. We propose the following mechanism, as shown in Scheme 8, to account for the products obtained in hexane and in THF. The routes (a) and (b) in Scheme 8 apply to the reaction in the non-polar solvent—hexane, whereas the routes (a), (b) and (c) for the reaction in the polar, coordinating solvent—THF (Scheme 9).

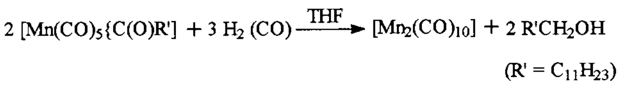
The CO dissociation from the alkoxycarbonyl complex [Mn(CO)$_5${C(O)OR}] may form the 16-electron intermediate [Mn(CO)$_4${C(O)OR}], which has been observed in the mass spectra of the alkoxycarbonyl complexes. The intermediate [Mn(CO)$_4${C(O)OR}] may undergo: (a) alkoxy group migration to form the alkoxy complex [Mn(CO)$_5$(OR)], which can then be protonated; (b) proton coordination followed by elimination to yield the formate; and (c) in the presence of the coordinating ligand THF, the solvent might be coordinated to the manganese centre yielding the THF-coordinated intermediate [Mn(CO)$_4$(THF){C(O)OR}]. Solvents-coordinated acyl complexes [Mn(CO)$_4$(S)-{C(O)R}] (S = DMSO and DMF) have been previously reported [19], and the THF-coordinated species [Mn(CO)$_5$(THF)]$^+$ has been proposed [14]. Direct evidence for the formation of the intermediate [Mn(CO)$_4$(THF){C(O)OR}] complex, however, has not been obtained.

## 3. Conclusion

A series of new long chain alkoxycarbonyl manganese pentacarbonyl complexes [Mn(CO)$_5${C(O)OR}] has been synthesized and fully characterized. The results of the reactions of manganese pentacarbonyl alkyl, acyl and alkoxycarbonyl complexes with syngas in hexane and THF show solvent effects. These reactions are relevant to catalytic reactions such as hydroformylation and the Fischer–Tropsch synthesis, where metal alkyl, acyl and alkoxycarbonyl species have been proposed as key intermediates.

## 4. Experimental

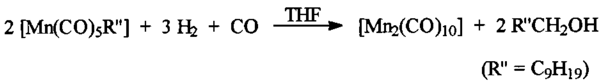
All reactions were carried out under an atmosphere of high purity nitrogen using standard Schlenk tube techniques unless otherwise stated. Tetrahydrofuran (THF) and hexane were dried by distilling over sodium/benezophonone. [Mn$_2$(CO)$_{10}$] was obtained from Strem Chemical Inc. and the compounds Cl(CO)(CH$_2$)$_n$CH$_3$ were obtained from Aldrich, and were used without further purification. Alumina (BDH, active neutral, Brockman grade I) was deactivated before use.



$$2\,[Mn(CO)_5\{C(O)R'\}] + 3\,H_2\,(CO) \xrightarrow{THF} [Mn_2(CO)_{10}] + 2\,R'CH_2OH$$

$$(R' = C_{11}H_{23})$$

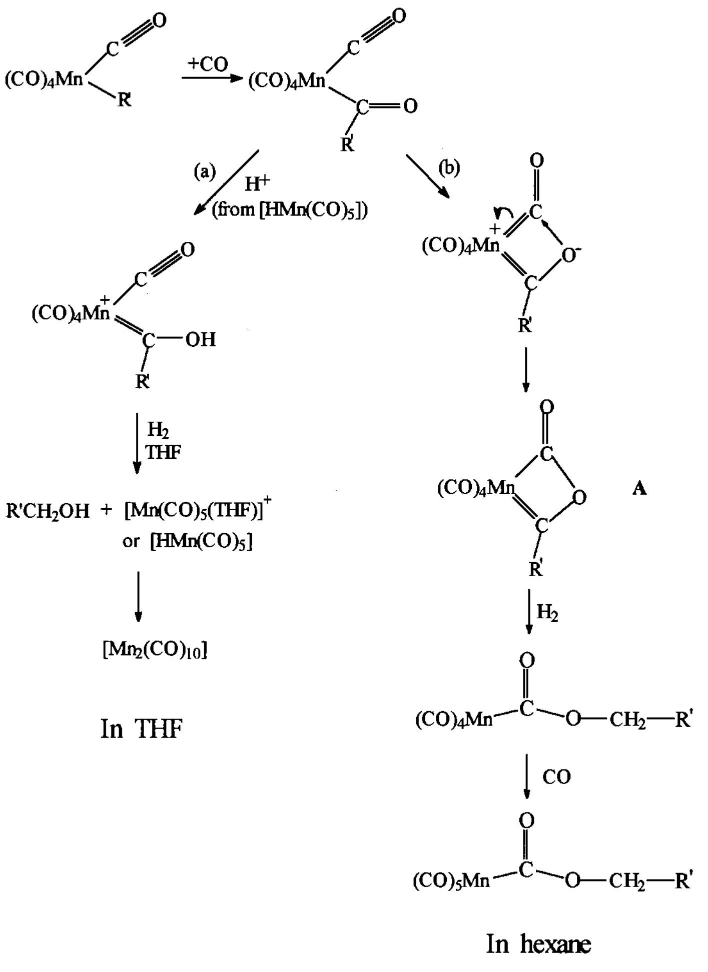
Scheme 4.



$$2\,[Mn(CO)_5R''] + 3\,H_2 + CO \xrightarrow{THF} [Mn_2(CO)_{10}] + 2\,R''CH_2OH$$

$$(R'' = C_9H_{19})$$

Scheme 5.



Scheme 6.

Melting points were recorded on a Kofler hot-stage microscope (Reichert-Thermovar) and are uncorrected. Differential scanning calorimetry (DSC) and thermal gravimetry analysis (TGA) were performed on a Perkin-Elmer PC Series 7 instrument under a nitrogen atmosphere with a heating rate of 10 or 20°C min$^{-1}$. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on either a Perkin-Elmer 983 or a Paragon 1000 FT-IR spectrophotometer in solution cells with NaCl windows.

$^1$H-NMR spectra were recorded on a Varian XR 200 (at 200 MHz) spectrometer or a Varian Unity 400 (at 400 MHz) spectrometer. $^{13}$C-NMR spectra were recorded on the Varian XR 200 (at 50 MHz) spectrometer or the Varian Unity 400 (at 100 MHz) spectrometer. The chemical shifts are relative to TMS (0 ppm) in the $^1$H and $^{13}$C-NMR spectra, where the deuterated solvent signals were used as references and the chemical shifts adjusted accordingly. Low resolution mass spectra were recorded with a VG Micromass 16F spectrometer operated at 70 eV ionizing voltage and using an accelerating voltage of 4 kV. All high pressure reactions were carried out in a 250 ml Berghoff autoclave.

The acyl complexes $[Mn(CO)_5\{C(O)R'\}]$ ($R' = n$-$C_6H_{13}$ to $n$-$C_9H_{19}$, $n$-$C_{11}H_{23}$, and $n$-$C_{15}H_{31}$) and the alkyl complexes $[Mn(CO)_5R'']$ ($R'' = n$-$C_8H_{17}$ and $n$-$C_{13}H_{27}$) were prepared according to the literature methods [11].

### 4.1. Synthesis of $[Mn(CO)_5\{C(O)OR\}]$ ($R = CH_2R'$)

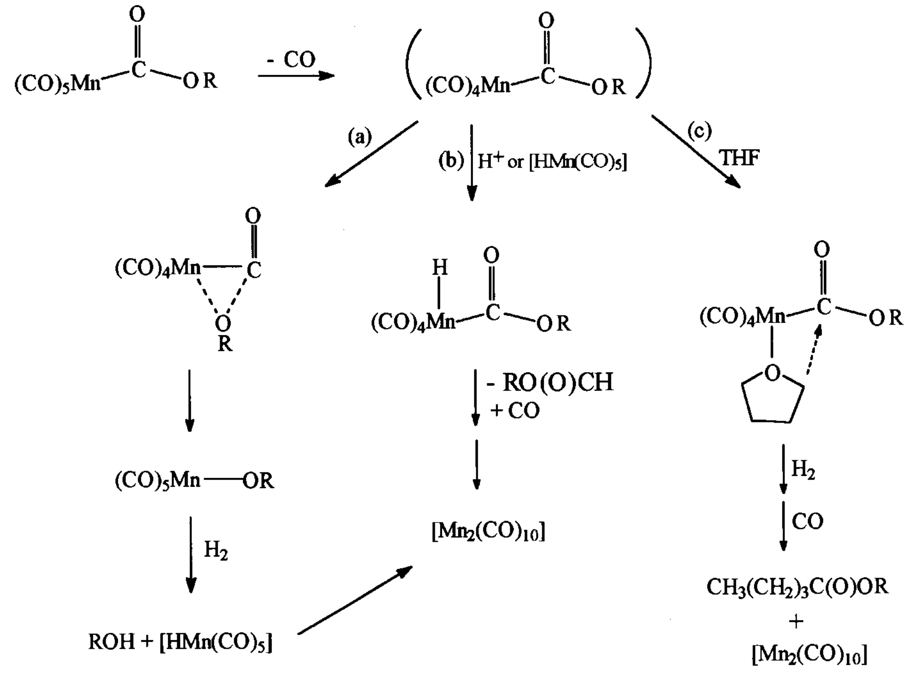
The complexes $[Mn(CO)_5\{C(O)OR\}]$ ($R = CH_2R'$, **1**–**4** and **7**) were synthesized by the reactions of the acyl complexes $[Mn(CO)_5\{C(O)R'\}]$ ($R' = n$-$C_6H_{13}$ to $n$-

$$2\,[Mn(CO)_5\{C(O)OR\}] + H_2\,(CO) \xrightarrow{\text{hexane}} [Mn_2(CO)_{10}] + RO(O)CH + ROH$$

Scheme 7.

$$2[Mn(CO)_5\{C(O)OR\}] + H_2\,(CO) \xrightarrow{\text{THF}} [Mn_2(CO)_{10}] + RO(O)CH + ROH + CH_3(CH_2)_3C(O)OR$$

Scheme 8.



Scheme 9.

$C_9H_{19}$, $n$-$C_{11}H_{23}$ and $n$-$C_{15}H_{31}$) with syngas ($CO/H_2$) in hexane according to the following general procedure.

In a typical reaction, the autoclave was charged with the acyl complex [$Mn(CO)_5\{C(O)R'\}$] (ca. 200 mg) in hexane (10 ml) with a stirrer bar in a flask and was sealed. The autoclave was filled with $CO/H_2$ (20 bar) and the gas vented. This procedure was repeated two more times and then the autoclave was pressurized with $CO/H_2$ until a total pressure of 40 bar was reached. The reaction mixture was then heated to ca. 60°C for 3 h. The autoclave was cooled to room temperature and the gases vented. The solvent was removed, leaving a yellow residue. This was then dissolved in a minimum amount of petroleum ether (b.p. 40–60°C) and the solution cooled to − 78°C to crystallize the product. The product was recrystallized again to give the alkoxycarbonyl complex [$Mn(CO)_5\{C(O)OR\}$] ($R = CH_2R'$) as an off-white microcrystalline solid.

The complex [$Mn(CO)_5\{C(O)OC_{12}H_{25}\}$], **5** was similarly prepared by the reaction of [$Mn(CO)_5$-$\{C(O)C_{11}H_{23}\}$] (2.50 g, 6.3 mmol) with $CO/H_2$ (45 bar) in hexane (20 ml) at 60°C, with a longer reaction time (15 h). Recrystallization from pentane twice at − 78°C gave **5** (2.35 g, 87%) as a white microcrystalline solid.

The complexes [$Mn(CO)_5\{C(O)OR\}$] ($R = n$-$C_9H_{19}$, **3** and $n$-$C_{14}H_{29}$, **6**) were also synthesized by the reaction of the alkyl complexes [$Mn(CO)_5R''\}$] ($R'' = n$-$C_8H_{17}$ and $n$-$C_{13}H_{27}$) with syngas in hexane using a similar procedure as described above.

### *4.2. Reactivity of alkyl complexes [Mn(CO)$_5$R''], acyl complexes [Mn(CO)$_5${C(O)R'}] and alkoxycarbonyl complexes [Mn(CO)$_5${C(O)OR}]*

#### *4.2.1. Reaction of the acyl complex [Mn(CO)$_5${C(O)C$_{11}$H$_{23}$}] with syngas in THF: synthesis of alcohol*

The reaction was carried out in an autoclave which was charged with [$Mn(CO)_5\{C(O)C_{11}H_{23}\}$] (0.20 g, 0.53 mmol) and THF (15 ml). The autoclave was sealed and filled with syngas to 20 bar and the gas vented. This procedure was repeated two more times. The autoclave was then pressurized with syngas to 48 bar. The solution was then heated at 60°C for 8 h with stirring. The autoclave was allowed to cool to room temperature and the gases vented. A yellow solution was obtained, which, after removing the solvent under vacuum, gave a yellow solid. The IR spectrum of the solvent that was removed showed two $\nu(CO)$ bands at 2020s, 1995s $cm^{-1}$, suggesting that the solvent contained a small amount ($< 5\%$) of [$HMn(CO)_5$] [29]. The yellow solid was dissolved in a minimum amount of $CH_2Cl_2$/pentane (25%) and chromatographed on a short silica gel column (7 cm x 2 cm). Elution with 5% $CH_2Cl_2$/pentane separated a yellow band, which, on evaporation of the solvent and drying under vacuum, yielded a yellow solid identified as [$Mn_2(CO)_{10}$] (0.097 g, 95%), on the basis of its IR spectrum ($\nu(CO)$ in Nujol mull, 2045s, 2013vs, 1983m $cm^{-1}$, these data are the same as the IR spectrum of authentic [$Mn_2(CO)_{10}$]). Elution with $CH_2Cl_2$ separated a second band which was colourless.

After removing the solvent and drying under vacuum, this gave an off-white solid (m.p. 24–27°C) which was identified as $n$-$C_{12}H_{25}OH$ (0.090 g, 92%; literature m.p. [30]: 26°C), on the basis of its IR, MS, $^1$H-NMR and $^{13}$C-NMR data. Low-resolution MS: 179 $(M-OH)^+$; IR $\nu$/cm$^{-1}$ (neat): 3343m, br ($\nu$OH), 2925s, 2854s [$\nu(CH_2+CH_3)$], 1466m, 1378w, 1056m, 720w; $^1$H-NMR ($CDCl_3$) $\delta$ (ppm): 3.88 (2H, b, $CH_2O$), 2.46 (1H, b, OH), 1.53 (2H, m, $CH_2CH_2O$), 1.25 (18H, b, 9 × $CH_2$), 0.86(3H, b, $CH_3$); $^{13}$C-NMR ($CDCl_3$) $\delta$ (ppm): 63.44 ($CH_2OH$), 32.94, 31.92, 29.62, 29.46, 29.35, 25.80, 22.68, 14.09 ($CH_3$). These data are in good agreement with the reported IR [31], $^1$H-NMR [32] and $^{13}$C-NMR [33] data.

### *4.2.2. Reaction of [Mn(CO)$_5${C(O)OC$_{12}$H$_{25}$}] with syngas in hexane at 85°C*

A solution of $[Mn(CO)_5\{C(O)OC_{12}H_{25}\}]$ (0.13 g, 0.32 mmol) in hexane (10 ml) in a flask was placed in an autoclave. The autoclave was sealed and filled with syngas to 20 bar and the gas vented. This procedure was repeated two more times. The autoclave was pressurized with syngas to 48 bar, then heated at 85°C for 11 h with stirring. The autoclave was allowed to cool to room temperature and the gases vented. A yellow solution was obtained, which, after removing the solvent under reduced pressure, gave a mixture of white and yellow solids. This mixture was dissolved in a minimum amount of $CH_2Cl_2$/hexane (5%) and chromatographed on a short silica gel column (7 × 2 cm). Three fractions were obtained. Elution with 5% $CH_2Cl_2$/hexane separated a yellow band. A yellow solid was obtained by evaporation of the solvent and drying under vacuum. The yellow solid was identified as $[Mn_2(CO)_{10}]$ (0.060 g, 96%) on the basis of its IR spectrum. The second band was colourless and gave an off-white solid $HCO_2C_{12}H_{25}$ (0.024 g, 33%), identified by mass spectroscopy, IR, $^1$H and $^{13}$C-NMR spectroscopy. The third fraction gave a white solid $n$-$C_{12}H_{25}OH$ (0.39 g, 66%), on the basis of its mass spectrum, IR, and $^1$H-NMR.

### *4.2.3. Reaction of [Mn(CO)$_5${C(O)OC$_{12}$H$_{25}$}] with syngas in THF*

A solution of $[Mn(CO)_5\{C(O)OC_{12}H_{25}\}]$ (0.20 g, 0.49 mmol) in THF (10 ml) in a flask was placed in an autoclave. The autoclave was sealed and filled with syngas to 20 bar and the gas vented. This procedure was repeated two more times. The autoclave was then pressurized with syngas to 48 bar. The solution was then heated at 60°C for 8 h with stirring. The autoclave was allowed to cool to room temperature and the gas vented. An IR spectrum of the reaction mixture showed that there was still unreacted starting material. The reaction was continued using the same conditions as above for additional 15 h. The autoclave was again allowed to cool to room temperature and the gas vented. The reaction had gone to completion and a yellow solution was obtained. After removing the solvent under vacuum, a mixture of white and yellow solids was obtained. The IR spectrum of the removing solution showed two $\nu$(CO) bands at 2019s, 1993s cm$^{-1}$, suggesting that the solution contained $[HMn(CO)_5]$ [29]. The solid mixture was dissolved in a minimum amount of $CH_2Cl_2$/pentane (5%) and chromatographed on a short silica gel column (7 cm × 2 cm). Four fractions were obtained. The first fraction, eluted with 5% $CH_2Cl_2$/pentane, was a yellow band. Evaporation of the solvent and drying under vacuum gave a yellow solid, which was identified as $[Mn_2(CO)_{10}]$ (0.06 g, 63%), on the basis of its IR spectrum. The other fractions were eluted with $CH_2Cl_2$. The second band gave a white solid product and was identified as $n$-$C_{12}H_{25}OH$ (0.04 g, 46%), on the basis of its IR spectrum and $^1$H-NMR. The next product was identified as an ester $CH_3(CH_2)_3CO_2(CH_2)_{11}CH_3$ (0.06 g, 43%), on the basis of its mass spectrum, IR, $^1$H and $^{13}$C-NMR. The last product was identified as $HCO_2C_{12}H_{25}$ (ca. 0.015 g, 12%), on the basis of its IR and $^1$H-NMR.

## Acknowledgements

We thank the University of Cape Town, SASOL and FRD for support.

## References

[1] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, 2nd ed., University Science Books, Mill Valley, CA, 1987, p. 633.

[2] J.B. Blackborow, R.J. Daroda, G. Wilkinson, Coord. Chem. Rev. 43 (1982) 17.

[3] C.D. Wood, P.E. Garrou, Organometallics 3 (1984) 170.

[4] P.J. Stang, Z. Zhong, Organometallics 11 (1992) 1026.

[5] D. Milstein, J.L. Huck, J. Am. Chem. Soc. 104 (1982) 6150.

[6] G. Vasapollo, L. Toniolo, G. Cavinato, F. Bigoli, M. Lanfranchi, M.A. Pellinghelli, J. Organomet. Chem. 481 (1994) 173.

[7] M. Tasi, G. Palyi, in: R.B. King, J.J. Eisch (Eds.), Organometallic Synthesis, vol. 4, Academic Press, New York, 1988, p. 266.

[8] R. Bertani, G. Cavinato, L. Toniolo, G. Vasapollo, J. Mol. Catal. 84 (1993) 165.

[9] R. Bertani, G. Cavinato, G. Facchin, L. Toniolo, A. Vavasori, J. Organomet. Chem. 466 (1994) 273.

[10] D. Carmona, J. Ferrer, J. Reyes, L.A. Oro, Organometallics 12 (1993) 4241.

[11] J.-A.M. Andersen, J.R. Moss, Organometallics 13 (1994) 5013.

[12] J.-A.M. Andersen, J.R. Moss, J. Organomet. Chem. 439 (1992) 25.

[13] J.-A.M. Andersen, J.R. Moss, Adv. Organomet. Chem. 37 (1995) 169.

[14] J.-A.M. Andersen, Ph.D. Thesis, University of Cape Town, Cape Town, South Africa, 1993.

[15] T. Kruck, M. Noack, Chem. Ber. 97 (1964) 1693.

[16] D.J. Sheeran, J.D. Arenivar, M. Orchin, J. Organomet. Chem. 316 (1986) 139.

[17] J.H. Freudenberger, M. Orchin, Organometallics 1 (1982) 1408.
[18] B.D. Dombek, J. Am. Chem. Soc. 101 (1979) 6466.
[19] T.L. Bent, J.D. Cotton, Organometallics 10 (1991) 3156.
[20] S.F. Mapolie, J.R. Moss, J. Chem. Soc. Dalton Trans, (1990) 299.
[21] P.L. Motz, D.J. Sheeran, M. Orchin, J. Organomet. Chem. 383 (1990) 201.
[22] P.L. Motz, D.M. Ho, M. Orchin, J. Organomet. Chem. 407 (1991) 259.
[23] R.B. Bedford, A.F. Hill, A.J.P. White, D.J. Williams, Angew. Chem. Int. Ed. Engl. 35 (1996) 95.
[24] R. Angelici, Acc. Chem. Res. 5 (1972) 335.
[25] N.A. Beach, H.B. Gray, J. Am. Chem. Soc. 90 (1968) 5713.
[26] I. Kovacs, C.D. Hoff, F. Ungvary, L. Marko, Organometallics 4 (1985) 1347.
[27] M.E. Dry, Catalysis Today 6 (1990) 183.
[28] G. Suss-Fink, J.-M. Soulie, G. Rheinwald, H. Stoeckli-Evans, Y. Sasaki, Organometallics 15 (1996) 3416.
[29] D.K. Huggins, H.D. Kaesz, J. Am. Chem. Soc. 86 (1964) 2734.
[30] R.C. Weast, M.J.A. Astle, CRC Handbook of Chemistry and Physics, 61st ed., CRC Press, Boca Raton, 1981.
[31] (a) N.B. Colthup, Introduction to Infrared and Raman Spectroscopy, Academic Press Inc., New York, 1990. (b) C.J. Pouchert, The Aldrich Library of Infrared Spectra, 3rd ed., Aldrich Chemical Company Inc., 1981.
[32] C.J. Pouchert, The Aldrich Library of-NMR Spectra, 2nd ed., Aldrich Chemical Company Inc., 1983.
[33] E. Breitmaier, W. Voelter, Carbon-13-NMR Spectroscopy, 3rd ed., VCH, Weinheim, 1987.