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Synthesis of an Extensive Series of Manganese Pentacarbonyl Alkyl and Acyl Compounds: Carbonylation and Decarbonylation Studies on [Mn(R)(CO)$_5$] and [Mn(COR)(CO)$_5$]

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The synthesis and characterization of the compounds [Mn(COR)(CO)$_5$] (R = CH_3 to n-C_9H_{19}, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$, n-$C_{15}H_{31}$, n-$C_{17}H_{35}$) and [Mn(R)(CO)$_5$] (R = CH_3 to n-$C_{18}H_{37}$) are reported. The majority of these compounds are new. Apart from the ethyl-, n-propyl-, and n-butylmanganese pentacarbonyls, the majority of the alkyl compounds are relatively stable to air and heat. A mechanism is proposed for the decomposition of the ethyl and n-propyl compounds. Kinetic studies have been carried out on the reactions [Mn(COR)(CO)$_5$] → [Mn(R)(CO)$_5$] + CO and [Mn(R)(CO)$_5$] + PPh$_3$ → *cis*-[Mn(COR)(CO)$_4$(PPh$_3$)], and it is found that the rates of both the carbonylation and decarbonylation reactions are dependent on the group R.

Introduction

The first reported synthesis of the simplest manganese pentacarbonyl alkyl species, *viz.* methylmanganese pentacarbonyl, was by Closson *et al.* in 1957.[1] In 1958, Hieber and Wagner reported the preparation of ethyl- and n-propylmanganese pentacarbonyls.[2] However, this group subsequently reported that the compound that they identified as ethylmanganese pentacarbonyl was in fact the propionyl derivative, [Mn(COC$_2$H$_5$)(CO)$_5$][3] (and presumably the n-propyl derivative they reported was in all probability the butanoyl species, [Mn(COC$_3$H$_7$)(CO)$_5$]). In this paper they described ethylmanganese pentacarbonyl as a yellow oil. The first "genuine" reported synthesis of n-propylmanganese pentacarbonyl was by Calderazzo and Cotton in 1962.[4] Both the ethyl and the propyl compounds were, however, found to be extremely unstable, decomposing in the dark, under vacuum at −10 °C.[5]

Some discrepancy exists in the literature as to the reasons for the instability of ethyl- (and n-propyl-) manganese pentacarbonyls. One school of thought seems to hold with the possibility that [Mn(C$_2$H$_5$)(CO)$_5$] may decompose *via* β-hydride alkene elimination, presumably to give [Mn(H)(CO)$_5$] and ethylene.[6–8] However, it has also been observed that [Mn(COC$_2$H$_5$)(CO)$_5$] is a decomposition product of [Mn(C$_2$H$_5$)(CO)$_5$][5,9–11] and the main decomposition pathway for [Mn(C$_2$H$_5$)(CO)$_5$] may thus involve carbonyl insertion.[12] This view is supported by the large rate constant measured for the carbonylation of [Mn(C$_2$H$_5$)(CO)$_5$].[4] The rate constant measured for the carbonylation of [Mn(n-C$_3$H$_7$)(CO)$_5$] was even larger than that measured for the ethyl derivative,[4] and n-propylmanganese pentacarbonyl is even less stable than ethylmanganese pentacarbonyl. It may therefore have been assumed that the n-butyl and higher alkyl homologues of manganese pentacarbonyl may be even more unstable. This assumption may have deterred further investigations into n-alkyl derivatives of manganese pentacarbonyl.

The particular questions we wished to address were (a) if the reason for the instability of ethylmanganese pentacarbonyl is a very facile and rapid carbonylation process, then would long chain alkyl (LCA) groups ($>$C4) migrate even faster than the short chain alkyl (SCA) groups ($\leq$C$_4$), resulting in even greater instability, or (b) would the rate of migratory insertion reach a peak at a particular chain length and then, due to steric factors, slow down, resulting in relatively stable compounds?

The majority of studies on transition metal alkyl complexes (L$_n$MR) as models for catalytic intermediates have involved SCA groups (R = CH_3, C_2H_5, n-C_3H_7), and there have been relatively few studies on the longer chain homologues. Studies on SCA complexes can, in particular, provide information on chain growth processes, whereas studies on LCA complexes may provide information more relevant to chain termination steps. The mechanism of these termination steps are important in catalytic reactions such as Ziegler–Natta polymerizations[13] and the Fisher–Tropsch process[14] where the preferential formation of a product of a particular carbon chain number may be desired. It has been shown that many reactions of transition metal alkyl

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complexes relevant to catalysis depend on the length of the alkyl chain.[15−18] Berke and Hoffman have also reported that activation parameters for alkyl migration in metal alkyl complexes depend on the number of carbon atoms in the alkyl chain.[19]

Numerous investigations into the rate of migratory carbonyl insertion (and the reverse reaction, decarbonylation) for $[Mn(R)(CO)_5]$ (R = SCA) have been carried out,[11,16,20−26] and all reports are in agreement with the finding that the rates for both carbonylation and decarbonylation follow the order R = *n*-Pr > Et > Me, and that the carbonyl insertion reaction proceeds by migration of the alkyl group onto an adjacent (*i.e. cis*) carbonyl ligand rather than by direct CO insertion.

However, study of the alkyl migration reaction in $[Mn(R)(CO)_5]$ (and the decarbonylation reaction in $[Mn(COR)(CO)_5]$) where R corresponds to an extensive homologous series of *n*-alkyl groups has never been reported, presumably due to the fact that *n*-alkyl derivatives were expected to be unstable.[11]

We have, however, been able to prepare such a series of acyl and *n*-alkyl derivatives of manganese pentacarbonyl and we now report our results on the synthesis and characterization of these compounds as well as on the reactivity of (a) $[Mn(COR)(CO)_5]$ compounds with respect to the decarbonylation reaction and (b) $[Mn(R)(CO)_5]$ compounds with respect to the carbonyl insertion reaction (R = CH_3 to n-C_9H_{19}, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$, n-$C_{15}H_{31}$, n-$C_{17}H_{35}$ (and R = n-$C_{18}H_{37}$ for $[Mn(R)(CO)_5]$ only)). Such a study is important since the alkyl migration reaction is a key step in many catalytic processes. We have reported some of our results in a preliminary communication.[27]

Results and Discussion

Acylmanganese Pentacarbonyl Compounds, $[Mn(COR)(CO)_5]$ (R = CH_3 to n-C_9H_{19}, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$, n-$C_{15}H_{31}$, and n-$C_{17}H_{35}$): **Synthesis and Characterization**. Acetyl-, **1** (R = CH_3),[28] propionyl-, **2** (R = C_2H_5),[28] butanoyl-, **3** (R = n-C_3H_7),-[11] and hexanoyl-, **5** (R = n-C_5H_{11})[29] manganese pentacarbonyl have been reported previously. They were all prepared by reaction of the manganese pentacarbonyl anion with the appropriate acyl chloride. We now report the synthesis of the new compounds $[Mn(COR)(CO)_5]$ where R = n-C_4H_9 (**4**), n-C_6H_{13} (**6**), n-C_7H_{15} (**7**), n-C_8H_{17} (**8**), n-C_9H_{19} (**9**), n-$C_{11}H_{23}$ (**10**), n-$C_{13}H_{27}$ (**11**), n-$C_{15}H_{31}$ (**12**), and n-$C_{17}H_{35}$ (**13**). These new compounds were all prepared as shown in eq 1.

$$Na[Mn(CO)_5] + RCOCl \xrightarrow[25\ °C]{THF} [Mn(COR)(CO)_5] + NaCl \quad (1)$$

Table 1. Data for $[Mn(COR)(CO)_5]$

R	compd no.	yield (%)	mp (°C)	elemental analysis	
				C found (calcd)	H found (calcd)
CH_3	**1**	61	54–55	35.1 (35.2)	1.4 (1.3)
C_2H_5	**2**	37	55–57	38.1 (38.1)	1.9 (2.0)
n-C_3H_7	**3**	38	45–47	41.1 (40.6)	2.8 (2.7)
n-C_4H_9	**4**	42	35–37	43.1 (42.9)	3.1 (3.2)
n-C_5H_{11}	**5**	43	33–35	44.7 (44.9)	3.9 (3.8)
n-C_6H_{13}	**6**	40	28–30	47.3 (46.8)	4.3 (4.3)
n-C_7H_{15}	**7**	38	29–31	48.6 (48.5)	4.9 (4.7)
n-C_8H_{17}	**8**	42	27–29	50.8 (50.0)	5.3 (5.1)
n-C_9H_{19}	**9**	46	28–29	53.2 (53.7)	5.2 (5.7)
n-$C_{11}H_{23}$	**10**	38	27–30	54.2 (54.0)	6.2 (6.1)
n-$C_{13}H_{27}$	**11**	29	36–39	56.0 (56.2)	6.3 (6.7)
n-$C_{15}H_{31}$	**12**	32	44–46	57.3 (58.1)	7.1 (7.2)
n-$C_{17}H_{35}$	**13**	38	48–50	59.5 (59.7)	7.5 (7.6)

Compounds **1**−**3** and **5** were also prepared by us in this manner. All the compounds (**1**−**13**) were isolated as pale yellow solids which are relatively stable, both to heat and to air. They are also fairly stable in solution when kept under nitrogen. They have been fully characterized by melting point, elemental analysis, IR, ^1H NMR, ^{13}C NMR, and mass spectrometry.[30] The melting points and elemental analyses are given in Table 1; the spectroscopic data are given in the supplementary material.

IR Spectra. The IR spectra in the $\nu(CO)$ region are in good agreement with the values previously reported for $[Mn(COR)(CO)_5]$ compounds[29,31] and show the expected number of peaks for $[M(COR)(CO)_5]$ species[32] at the following approximate frequencies: A_1 (2112 cm^{-1}), B (2048 cm^{-1}), E (2006 cm^{-1}), A_1 (2000 cm^{-1}), and acyl (1658 cm^{-1}). There is no significant variation in $\nu(CO)$ upon changing the length of the alkyl chain.

NMR Spectra. Separate resonances are observed for the methyl protons of the alkyl chain and the α and β protons in these acyl complexes. The remaining methylene protons appear as a broad singlet. There is no significant variation in chemical shift with variation in the length of the alkyl chain, and integration is thus the only way to distinguish between these compounds using ^1H NMR measurements. The same was found for analogous rhenium acyl complexes[33] and related iron and ruthenium LCA compounds.[34]

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(30) *e.g.* for $[Mn\{CO(n\text{-}C_6H_{13})\}(CO)_5]$: IR ($\nu(CO)$ in hexane) 2111 (w), 2048 (w), 2006 (s), 2000 (s), 1652 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 6H, $MnCOCH_2CH_2(CH_2)_3$), 1.45 (m, 2H, $MnCOCH_2CH_2$), 2.89 (t, 2H, $MnCOCH_2$); ^{13}C NMR ($CDCl_3$) δ 13.86 (CH_3, *i.e.* C_6), 22.38 (C_5), 24.28 (C_4), 28.50 (C_3), 31.53 (C_2), 67.30 (C_1, *i.e.* $MnCOCH_2$), 210 (terminal carbonyls). For $[Mn\{CO(n\text{-}C_{17}H_{35})\}(CO)_5]$: IR ($\nu(CO)$ in hexane) 2112 (w), 2048 (w), 2006 (s), 2000 (s), 1658 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3H, CH_3), 1.24 (s, 28H, $MnCOCH_2CH_2(CH_2)_{14}$), 1.48 (m, 2H, $MnCOCH_2CH_2$), 2.90 (t, 2H, $MnCOCH_2$); ^{13}C NMR ($CDCl_3$) δ 15.49 (CH_3, *i.e.* C_{17}), 24.08 (C_{16}), 25.81 (C_{15}), 26.38 (C_{14}), 30.33−31.08 (C_{13}−C_3), 35.72 (C_2), 68.80 (C_1, *i.e.* $MnCOCH_2$), 212 (terminal carbonyls).

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The terminal carbonyl resonances are at the usual positions.[35] No variation in chemical shift was observed with an increase in the length of the alkyl chain. For compounds **1**–**8**, all the carbon atoms of the alkyl chain were assigned, whereas for compounds **9**–**13** the peaks due to the central methylene carbon atoms were not resolved. When compared to the ^{13}C NMR spectra of the starting acyl chlorides,[33] it is apparent that the manganese atom only exerts an influence on the first two carbon atoms of the alkyl chain.

Mass Spectra. The mass spectra of **1**–**13** are all similar and relatively simple. Most of them show parent molecular ions, and the major fragmentation pathway is sequential loss of terminal carbonyl groups followed by sequential loss of methylene fragments.

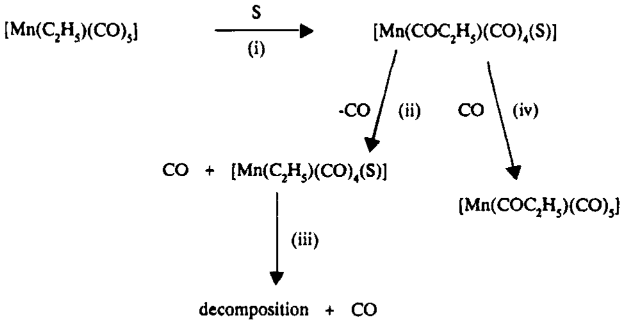
All spectra exhibit most of the peaks characteristic of manganese pentacarbonyl species, *viz.* the ions $[Mn(CO)_5]^+$ (*m/e* 195), $[Mn(CO)_2]^+$ (*m/e* 111), $[Mn(CO)]^+$ (*m/e* 83), $[MnH]^+$ (*m/e* 56), $[Mn]^+$ (*m/e* 55), and $[CO]^+$ (*m/e* 28).

Alkylmanganese Pentacarbonyl Compounds, $[Mn(R)(CO)_5]$ (R = CH_3 to n-$C_{18}H_{37}$); **Synthesis and Characterization.** Very few *n*-alkyl derivatives of manganese pentacarbonyl have ever been reported. The only examples in the literature are the methyl,[1] ethyl,[2–5] and *n*-propyl[4] derivatives. The reason for this scarcity is presumably a result of the extremely high instability of $[Mn(C_2H_5)(CO)_5]$, as reported by Green and Nagy.[5] It has thus been suggested that higher *n*-alkyl derivatives of manganese pentacarbonyl may be subject to the same instability.[36] However, if the reason for the instability of $[Mn(C_2H_5)(CO)_5]$ is a very rapid carbonylation process rather than β-hydride elimination (which seems possible, since the following compounds containing β-hydrogens are known and are all relatively stable: $[Mn\{CH_2CH(Ph)(CH_3)\}(CO)_5]$,[23] $[Mn(CH_2CH_2Ph)(CO)_5]$,[37] $[Mn\{CH_2CH_2CH{=}C(Ph)(CH_3)\}(CO)_5$,[38] and $[Mn\{CH(CH_3)CH{=}CHCH_3\}(CO)_5]$[39]), then LCA derivatives of manganese pentacarbonyl may very well be stable if they undergo carbonylation at a slower rate. This is indeed found to be the case, and we now report the synthesis, characterization, and reactivity of the homologous series of compounds $[Mn(R)(CO)_5]$, where R is CH_3 to n-$C_{18}H_{37}$ (**14**–**31**). This now represents, to our knowledge, the most extensive series of *n*-alkyl complexes of a transition metal. We also propose a possible mechanism for the decomposition of ethylmanganese pentacarbonyl in solution, as outlined in Scheme 1.

Thus, CO that is produced in steps ii and iii is used in step iv to carbonylate the solvated acyl intermediate. Step ii will proceed *via* loss of CO to form the intermediate species $[Mn(COC_2H_5)(CO)_3(S)]$ (which will then rearrange to $[Mn(C_2H_5)(CO)_4(S)]$). The formation of this intermediate species will be the rate-determining step in this decomposition process.

With the exception of the methyl (**14**), ethyl (**15**), and *n*-propyl (**16**) derivatives, all of the compounds synthesized by us are new. The majority of the compounds are stable both to heat and to air for short periods of time.

Scheme 1[a]



[a] S = a molecule of solvent, *e.g.* THF.

The compounds with R = C_2H_5 to n-C_9H_{19}, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$, n-$C_{15}H_{31}$, and n-$C_{17}H_{35}$ were synthesized by thermal decarbonylation of the acyl precursors, as shown in eq 2.

$$[Mn(COR)(CO)_5] \xrightarrow[\text{reflux}]{\text{hexane}} [Mn(R)(CO)_5] + CO \quad (2)$$

For R = CH_3, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, n-$C_{14}H_{29}$, n-$C_{16}H_{33}$, and n-$C_{18}H_{37}$, the compounds were synthesized by reactions of $Na[Mn(CO)_5]$ with the appropriate *n*-alkyl bromide (or methyl iodide for the methyl derivative), as shown in eq 3.

$$Na[Mn(CO)_5] + RBr \xrightarrow[25\,°C]{\text{THF}} [Mn(R)(CO)_5] + NaBr \quad (3)$$

The synthetic pathway represented by eq 3 was previously thought to be inaccessible, as it might be envisaged that a coordinating solvent such as THF would induce decomposition of the metal alkyl species as shown in steps i–iii of Scheme 1. However, since the alkyl migration process in these LCA derivatives is shown to be much slower than for the shorter chain analogues (see later), the mode of decomposition outlined in Scheme 1 is not easily accessible for LCA species.

The majority of compounds synthesized in this study were fully characterized by melting points, elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry.[40] The melting points and elemental analyses are given in Table 2; the spectroscopic data are given in the supplementary material. The ethyl, *n*-propyl, and *n*-butyl derivatives proved too unstable to obtain reliable results for elemental analysis, ^{13}C NMR, and mass spectrometry.

IR Spectra. As was observed with the acyl compounds, $[Mn(COR)(CO)_5]$, the IR data in the ν(CO) region for $[Mn(R)(CO)_5]$ show no significant variation upon changing the length of the alkyl chain. These data

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(40) *e.g.* for $[Mn(n\text{-}C_6H_{13})(CO)_5]$: IR ($\nu$(CO) in hexane) 2104 (w), 2007 (s), 1988 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, CH_3), 1.32 (s, 6H, $MnCH_2CH_2(CH_2)_3$), 1.70 (br, 2H, $MnCH_2CH_2$), 1.05 (t, 2H, $MnCH_2$); ^{13}C NMR ($CDCl_3$) δ 15.77 (CH_3, *i.e.* C_6), 24.52 (C_5), 31.02 (C_4), 36.10 (C_3), 37.16 (C_2), 6.80 (C_1, *i.e.* $MnCH_2$), 215 (terminal carbonyls). For $[Mn(n\text{-}C_{17}H_{35})(CO)_5]$: IR ($\nu$(CO) in hexane) 2104 (w), 2006 (s), 1988 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, CH_3), 1.26 (s, 28H, $MnCH_2CH_2(CH_2)_{14}$), 1.64 (br, 2H, $MnCH_2CH_2$), 1.03 (t, 2H, $MnCH_2$); ^{13}C NMR ($CDCl_3$) δ 14.03 (CH_3, *i.e.* C_{17}), 22.62 (C_{16}), 29.10–29.62 (C_{15}–C_5), 31.85 (C_4), 35.01 (C_3), 37.24 (C_2), 7.03 (C_1, *i.e.* $MnCH_2$), 213 (terminal carbonyls).

Table 2. Data for $[\mathrm{Mn(R)(CO)_5}]$

				elemental analysis	
R	cmpd no.	yield (%)	mp (°C)	C found (calcd)	H found (calcd)
CH_3	**14**	64	93–95	34.2 (34.3)	1.3 (1.4)
C_2H_5	**15**	28	oil	^{a}	
n-C_3H_7	**16**	32	oil	^{a}	
n-C_4H_9	**17**	31	oil	^{a}	
n-C_5H_{11}	**18**	52	oil	44.8 (45.1)	4.0 (4.2)
n-C_6H_{13}	**19**	63	oil	47.3 (47.2)	4.6 (4.7)
n-C_7H_{15}	**20**	64	oil	49.0 (49.0)	4.8 (5.1)
n-C_8H_{17}	**21**	80	oil	50.5 (50.7)	5.5 (5.6)
n-C_9H_{19}	**22**	92	oil	52.6 (52.2)	5.8 (5.9)
n-$C_{10}H_{21}$	**23**	31	oil	54.2 (53.6)	6.6 (6.3)
n-$C_{11}H_{23}$	**24**	88	oil	54.8 (54.9)	6.7 (6.6)
n-$C_{12}H_{25}$	**25**	50	36–40	56.2 (56.0)	6.8 (6.9)
n-$C_{13}H_{27}$	**26**	84	30–32	57.2 (57.1)	7.1 (7.2)
n-$C_{14}H_{29}$	**27**	56	37–41	58.2 (58.2)	7.3 (7.4)
n-$C_{15}H_{31}$	**28**	78	31–33	58.7 (59.1)	7.6 (7.7)
n-$C_{16}H_{33}$	**29**	48	42–45	60.2 (60.0)	7.8 (7.9)
n-$C_{17}H_{35}$	**30**	89	35–37	60.5 (60.8)	7.9 (8.1)
n-$C_{18}H_{37}$	**31**	51	41–44	61.5 (61.6)	8.2 (8.3)

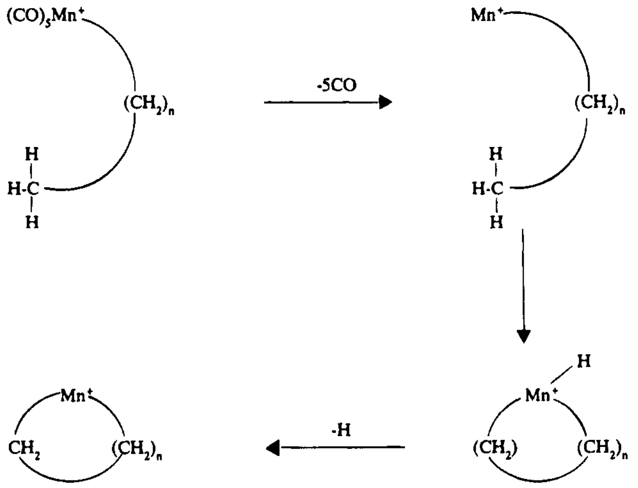
^{a} Compounds too unstable for elemental analysis.

are also in good agreement with those predicted for $[\mathrm{M(R)(CO)_5}]$ species,[32] showing peaks at the following approximate frequencies: A_1 (2105 cm^{-1}), E (2008 cm^{-1}), and A_1 (1988 cm^{-1}).

NMR Spectra. As was the case with the acyl compounds, separate resonances are seen only for the methyl protons and the α and β protons of the alkyl chain. The α protons are shielded by the metal, resulting in a signal at *ca.* 1.02 ppm. The remaining (central) methylene protons appear as one broad signal. There is no significant variation in chemical shift of any of the peaks when changing the length of the alkyl chain. Thus, integration is the only way to distinguish between these compounds using ^{1}H NMR measurements, as is the case with the acyl precursors.

The carbonyl resonances in the ^{13}C NMR spectra were at the expected positions[35] but were not resolved. This is, however, to be expected for $[\mathrm{Mn(R)(CO)_5}]$ species due to the quadrupolar manganese atom.[41] The carbonyl resonances also showed no variation in chemical shift when the chain length of the alkyl group was altered. For compounds **18**–**21** (*i.e.* R = n-pentyl to n-octyl) all of the carbon atoms of the alkyl chain gave rise to separate resonances. This was also the case for the acyl homologues. However, for R = n-nonyl onward, the peaks due to the central methylene carbon atoms were not resolved. Separate resonances were observed only for the methyl carbon atom, the adjacent methylene carbon atom (*i.e.* CH_2CH_3), and the α, β, γ, and δ carbon atoms (*i.e.* C_1 to C_4) of the alkyl chain. Beyond C_3, the ^{13}C NMR spectra of corresponding acyl and alkyl compounds are very similar, although this is hardly surprising.

Scheme 2



Mass Spectra. All the mass spectra that were obtained were similar and relatively simple. They all showed weak parent molecular ions with the major fragmentation pathway being sequential loss of carbonyl groups followed by sequential loss of methylene fragments. This fragmentation pattern is in good agreement with that proposed by Mays and Simpson[42] for the compounds $[\mathrm{Mn(R)(CO)_5}]$ where R = CH_3, C_6H_5, CF_3, and SO_2CH_3. The high-resolution mass spectrum of **30**, $[\mathrm{Mn\{(CH_2)_{17}CH_3\}(CO)_5}]$, showed some interesting features, *viz.* that weak peaks at *m/e* values corresponding to $[M - 5CO - H]^+$ and $[M - 5CO - 2H]^+$ were observed. Very weak peaks corresponding to $[M - 5CO - H]^+$ were also seen in the low-resolution mass spectra of compounds **24**, **26**, and **27**. A similar phenomenon has been observed for related iron alkyl compounds.[43,44] The reason for this fragmentation pattern may be a type of "remote functionalization" whereby a C–H bond of the methyl group of the alkyl chain is activated by the coordinatively unsaturated metal atom to give a metallacyclic species,[44] as shown in Scheme 2. Further loss of hydride could occur by β-hydride elimination without cleavage of the remaining alkyl residue. This mechanism enables C–H activation to occur at positions that are initially remote from the metal atom.

All mass spectra exhibited peaks characteristic of $[\mathrm{Mn(R)(CO)_5}]$ species, *viz.* $[\mathrm{Mn(CO)_5}]$ (*m/e* 195), $[\mathrm{Mn(CO)_4}]^+$ (*m/e* 167), $[\mathrm{Mn(CO)_3}]^+$ (*m/e* 139), $[\mathrm{Mn(CO)_2}]^+$ (*m/e* 111), $[\mathrm{Mn(CO)}]^+$ (*m/e* 83), $[\mathrm{MnH}]^+$ (*m/e* 56), $[\mathrm{Mn}]^+$ (*m/e* 55), and $[\mathrm{CO}]^+$ (*m/e* 28).

Rate Studies on the Decarbonylation Reaction for Acylmanganese Pentacarbonyl Compounds, $[\mathrm{Mn(COR)(CO)_5}]$ (R = CH_3 to n-C_9H_{19}, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$, n-$C_{15}H_{31}$, n-$C_{17}H_{35}$). Thermal decarbonylation, as shown in eq 4, is one of the most general routes to hydrocarbyl and perfluoroalkyl derivatives of manganese pentacarbonyl.

$$[\mathrm{Mn(COR)(CO)_5}] \xrightarrow{\Delta} [\mathrm{Mn(R)(CO)_5}] + \mathrm{CO} \qquad (4)$$

Based on the initial studies of Calderazzo and Cotton,[4,26] Booth *et al.*,[45] and later studies of Cawse *et al.*,[16] the mechanistic scheme as outlined in Scheme 3 was proposed.

In polar or coordinating solvents, the intermediate, $[\mathrm{Mn(COR)(CO)_4}]$, probably exists as a solvated hexacoordinate species, *viz.* $[\mathrm{Mn(COR)(CO)_4(S)}]$. Labeling studies using $[\mathrm{Mn(^{13}COCH_3)(CO)_5}]$[22] have shown that the molecule of CO which is lost is a terminal carbonyl group, and the rate-determining step is loss of this group. The ease of decarbonylation will therefore

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(41) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *80*, C31.

(42) Mays, M. J.; Simpson, R. N. F. *J. Chem. Soc. A* **1967**, 1936.

(43) Stone, J. A.; Laycock, D. E.; Lin, M.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1980**, 2488.

(44) Schwarz, H. *Acc. Chem. Res.* **1989**, *22*, 282.

(45) Booth, B. L.; Haszeldine, R. N.; Woffenden, N. P. *J. Chem. Soc. A* **1970**, 1979.

Scheme 3

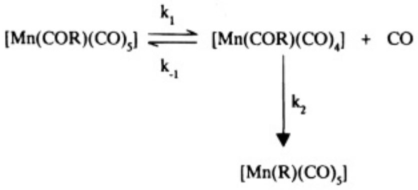


Table 3. Kinetic Data for the Decarbonylation of $[Mn(COR)(CO)_5]$ at 55.5 °C in Hexane[a]

R	$10^{-4}\,k_1$ (s)	$t_{1/2}$ (min)
CH_3	1.40	82.5
C_2H_5	2.00	57.8
n-C_3H_7	2.59	44.6
n-C_4H_9	3.09	37.4
n-C_5H_{11}	3.02	38.3
n-C_6H_{13}	2.95	39.2
n-C_7H_{15}	2.57	45.0
n-C_8H_{17}	2.38	48.5
n-C_9H_{19}	2.26	51.2
n-$C_{11}H_{23}$	1.97	58.6
n-$C_{13}H_{27}$	1.38	83.7
n-$C_{15}H_{31}$	0.94	122.9
n-$C_{17}H_{35}$	0.70	165.0

[a] Uncertainty parameters are in the region of 4%.

depend on the strength of the manganese to terminal carbonyl bond, which will be influenced to some extent by the nature of R. If one assumes a steady-state concentration of $[Mn(COR)(CO)_4]$ in Scheme 3, then one obtains the following rate equation:

$$\frac{\mathrm{d}[[Mn(R)(CO)_5]]}{\mathrm{d}t} = \frac{k_1 k_2[[Mn(COR)(CO)_5]]}{k_{-1}[CO] + k_2} \qquad (5)$$

Since the term $k_{-1}[CO]$ is usually very small, eq 5 simplifies to

$$\frac{\mathrm{d}[[Mn(R)(CO)_5]]}{\mathrm{d}t} = k[[Mn(COR)(CO)_5]] \qquad (6)$$

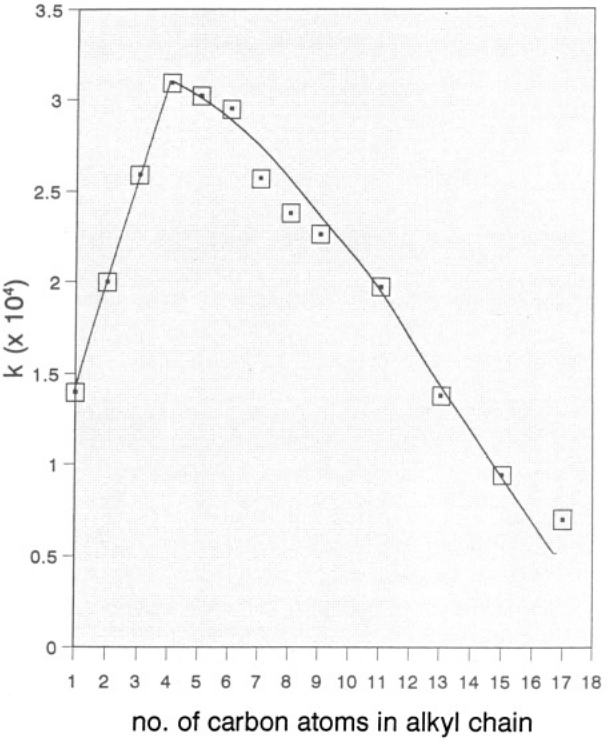
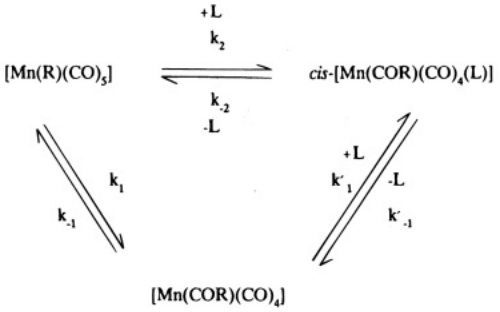


Figure 1. Plot of k versus the number of carbon atoms in the alkyl chain for the decarbonylation of $[Mn(COR)(CO)_5]$ (with error blocks shown).

In our studies, typically, a 0.04 M solution of $[Mn(COR)(CO)_5]$ was thermally decarbonylated in hexane at 55.5 °C. The reactions were followed by IR spectroscopy, and the kinetic data for the reaction are presented in Table 3. A plot of the number of carbon atoms in the alkyl chain of $[Mn(COR)(CO)_5]$ *versus* k is shown in Figure 1. Figure 1 shows that the rate of decarbonylation initially increases from $n = 0$ to $n = 3$ (*i.e* R = methyl to n-butyl) but then decreases steadily and then fairly rapidly through the series from $n = 4$ to $n = 16$ (*i.e.* R = n-pentyl to n-heptadecyl). This can be explained by a combination of steric and electronic effects, as follows: Up until $n = 3$ electronic effects predominate with the electron-donating ability of R following the order R = n-butyl > n-propyl > ethyl > methyl. Electron-donating groups should facilitate the decarbonylation process since they will stabilize the electron-deficient metal atom which is short of electrons due to two electrons being lost with the departing CO molecule. However, when $n > 3$, the electronic effect exerted by the alkyl group becomes more or less constant and steric effects start to take over. The larger alkyl groups (a) can conceivably exert more steric hindrance to the departing CO molecule in the rate-determining step and (b) may themselves encounter greater steric hindrance in the alkyl migration (k_2 step) of the reaction.[46] Thus, the overall rate is slower for LCA groups.

Rate Studies on the Carbonyl Insertion Reaction for Alkylmanganese Pentacarbonyl Compounds $[Mn(R)(CO)_5]$ (R = CH_3 to n-C_9H_{19}, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$, n-$C_{15}H_{31}$, n-$C_{17}H_{35}$, n-$C_{18}H_{37}$). Early studies by Calderazzo and co-workers,[4,23,26,47] Mawby *et al.*,[48] and later by Cawse *et al.*[16] have provided most of the mechanistic information on this process, and the following scheme (Scheme 4) is now generally accepted.

Scheme 4



The rate-determining step is alkyl migration to form the intermediate, $[Mn(COR)(CO)_4]$, which, in polar or coordinating solvents, exists as $[Mn(COR)(CO)_4(S)]$.[11,48-51] A solvated acyl species was also shown to be an

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[46] It was pointed out by a reviewer that if the larger alkyl groups do indeed exert more steric hindrance, then the $k_{-1}[CO]$ term in eq 5 may become appreciable and eq 5 would thus not simplify to eq 6. While we agree with this proposal, we are still of the opinion that eq 6 holds true, as the range of k values (Table 3) is very small. Thus, the overall effect of changing the alkyl groups is, in this instance, very small.

[47] Calderazzo, F.; Cotton, F. A. *Chim. Ind. (Milan)* **1964**, *46*, 1165.

[48] Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994.

[49] Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619.

Table 4. Kinetic Data for the Reaction of $[Mn(R)(CO)_5]$ with PPh_3 at 32.0 °C in Hexane[a]

R	10^4k_{obs} (s)	$t_{1/2}$ (min)
CH_3	0.63	182.8
C_2H_5	3.26	35.5
n-C_3H_7	6.37	18.1
n-C_4H_9	4.14	27.0
n-C_5H_{11}	2.83	40.8
n-C_6H_{13}	2.21	52.3
n-C_7H_{15}	2.02	52.5
n-C_8H_{17}	2.01	57.5
n-C_9H_{19}	1.99	58.0
n-$C_{11}H_{23}$	1.96	58.9
n-$C_{13}H_{27}$	1.91	60.5
n-$C_{15}H_{31}$	1.89	61.1
n-$C_{17}H_{35}$	1.85	62.4
n-$C_{18}H_{37}$	1.84	62.8

[a] Uncertainty parameters are in the region of 4%.

intermediate in polar solvents for alkyl migration reactions of a related molybdenum alkyl system.[52] Under the conditions of our experiments, there was no detectable contribution from the direct reaction path (k_2 step, Scheme 4).

The reactions we studied all proceeded to completion, and under the pseudo-first-order conditions enforced by an excess of L (in our case, L was PPh_3) relative to $[Mn(R)(CO)_5]$, the observed rate constant, k_{obs}, is given by eq 7.

$$k_{obs} = \frac{k_1k'_1[L]}{k_{-1} + k'_1[L]} \qquad (7)$$

The large molar excess of a ligand with high nucleophilicity, such as PPh_3, means that the reactive intermediate is more effectively captured by L than it reverts to the alkyl complex. Thus, for high nucleophilicity and at high concentrations of L, $k'_1[L] \gg k_{-1}$ and the reaction is pseudo first-order with k_{obs} approximating k_1. The latter, within the validity of the assumptions, is the rate constant for the formation of the acyltetracarbonyl intermediate.

This approach, *i.e.* the use of a large molar excess of a ligand of high nucleophilicity in order to impose first-order conditions on the reaction, has been applied extensively in kinetic studies of $[Mn(R)(CO)_5]$ species.[11,36,48,51–54] A detailed analysis of rate equations derived from Scheme 4 is given in a review article.[55] The reaction being followed is thus

$$[Mn(R)(CO)_5] + PPh_3 \xrightarrow{k_{obs}} cis\text{-}[Mn(COR)(CO)_4(PPh_3)] \qquad (8)$$

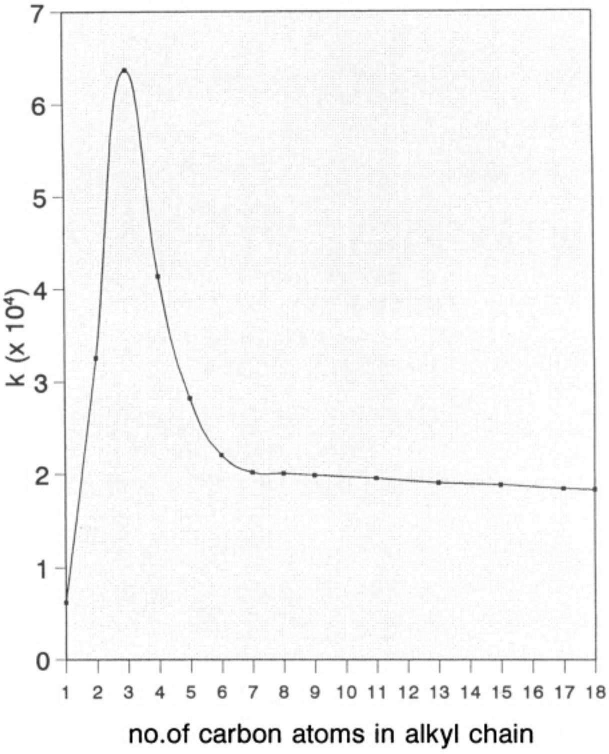

Figure 2. Plot of k versus the number of carbon atoms in the alkyl chain for the reaction of $[Mn(R)(CO)_5]$ with PPh_3.

All the reactions were followed by IR spectroscopy, and the kinetic data are presented in Table 4. A plot of the number of carbon atoms in the alkyl chain of $[Mn(R)(CO)_5]$ *versus* k_{obs} is given in Figure 2. Figure 2 shows that the rate of alkyl migration/carbonyl insertion initially increases for $n = 1$ to $n = 3$ (*i.e* R = CH_3 to n-propyl), then decreases rapidly until $n = 7$ (R = n-heptyl), and thereafter levels off, decreasing very slowly until $n = 17$ (R = n-octadecyl). As for the decarbonylation reaction, this reactivity pattern can be explained by a combination of steric and electronic effects. It is known that electron-donating substituents facilitate the alkyl migration reaction,[4,16,26] and this is indeed the case as the rate increases for R = CH_3 to n-C_3H_7; *i.e.* the R group is becoming more electron-donating in nature which results in rate acceleration. However, when R becomes larger than n-propyl, the electronic effect is more or less constant and steric effects start to take over, with rate retardation being observed. This occurs until R = n-heptyl, when the steric effects exerted by the alkyl group also become more or less constant and the addition of extra methylene (CH_2) groups has an almost negligible effect on the reaction rate. With an error limit of 4%, the values of k_{obs} for alkyl groups larger than n-heptyl are statistically identical, which can be seen in Figure 2—after R = n-heptyl, the graph virtually flattens out. Thus, the effect of the alkyl group is felt most strongly from R = CH_3 to R = n-C_7H_{15}.

This combination of steric and electronic factors that we have observed in the alkyl migration reactions of these manganese complexes may pertain to other alkyl complexes and also to alkyl intermediates in catalytic reactions. It could thus serve as a possible explanation for the observed deviation from the predicted Schulz–Flory product distribution above C_{12} in the Fischer–Tropsch synthesis.[56] The fact that a lower proportion than was initially predicted of higher carbon-numbered products ($>C_{12}$) is obtained in the Fischer–Tropsch reaction has been attributed to the lower mobility of

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(50) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34.

(51) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345.

(52) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

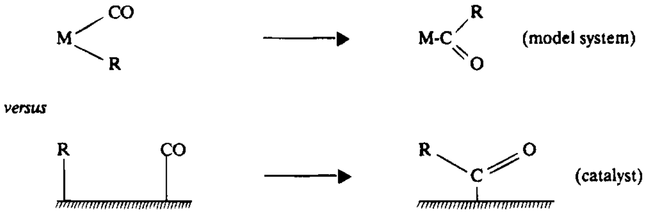
(53) Cotton, J. D.; Kroes, M. M.; Markwell, R. D.; Miles, E. A. *J. Organomet. Chem.* **1990**, *388*, 133.

(54) Cotton, J. D.; Markwell, R. D. *Organometallics* **1985**, *4*, 937.

(55) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87.

(56) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136.

Scheme 5



these larger hydrocarbon groups.[56] We have now shown this to be the case with these manganese alkyl model complexes. Thus, the alkyl migration process as observed with these complexes could be regarded as a model for a step leading to chain termination in catalytic polymerization reactions. The reaction which interrupts chain growth and results in the formation of hydrocarbon oligomers is possibly a chain transfer reaction in the course of which the alkyl chain leaves the metal. It could, however, also be a model for alkyl migration in chain growth processes, as represented in Scheme 5.

Tables 3 and 4 show that the rates of CO insertion span a larger range than the rates for the decarbonylation process. This is not unexpected, since the rate-determining step in the CO insertion reaction is the migration of R, whereas in the decarbonylation reaction it is loss of a terminal carbonyl group. It is thus understandable that the CO insertion process is more strongly affected by R than is the decarbonylation reaction. However, the manganese to terminal carbonyl bond strength is affected by the rest of the molecule and thus will be affected to some extent by R. The rate of decarbonylation does not level off, even with very large R groups. This can be explained by the proposal that, if the rate-determining step is loss of a terminal CO, the CO group has to dissociate from the rest of the molecule completely and will thus continue to be affected by larger and larger R groups. Larger R groups will make it increasingly difficult for the molecule of CO to completely remove itself from the increasingly larger coordination sphere of the metal.

Conclusions

Extensive series of acyl and *n*-alkyl compounds of the types $[Mn(COR)(CO)_5]$ and $[Mn(R)(CO)_5]$ have been synthesized and fully characterized. Contrary to previous expectations, the majority of these compounds are relatively stable. Kinetic analysis of the decarbonylation and CO insertion reactions show that the reactivity patterns of the above compounds are determined by a subtle balance between the electronic and steric effects exerted by R. These results may pertain to intermediates in catalytic reactions.

Experimental Section

All reactions were carried out under an atmosphere of high-purity nitrogen using standard Schlenk-tube techniques. Tetrahydrofuran (THF) and hexane were distilled over sodium before use. The compounds $Br(CH_2)_nCH_3$ and $ClCO(CH_2)_nCH_3$ were obtained from Aldrich and were used without further purification. Methyl iodide, CH_3I, was obtained from Merck. $[Mn_2(CO)_{10}]$ was obtained from Strem. Alumina (BDH, active neutral, Brockman grade 1) was deactivated prior to use. Melting points were determined on a Kofler hotstage 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 in solution cells with NaCl windows. ^1H and ^{13}C NMR spectra were recorded on a Varian XR200-MHz spectrometer. Tetramethylsilane (TMS) was used as an internal reference standard. 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. The source temperature was initially 20–30 °C and was raised to *ca.* 200 °C during data collection. The data were analyzed on a VG200 digital data system. High-resolution mass spectra were recorded on an AEI MS 902 mass spectrometer.

(a) General Route to the Compounds $[Mn(COR)(CO)_5]$ (R = CH_3 to *n*-C_9H_{19}, *n*-$C_{11}H_{23}$, *n*-$C_{13}H_{27}$, *n*-$C_{15}H_{31}$, *n*-$C_{17}H_{35}$). A solution of $Na[Mn(CO)_5]$ (10.6 mmol) (prepared by reductive cleavage of $[Mn_2(CO)_{10}]$ over Na/Hg) in THF (30 mL) was added dropwise over *ca.* 10 min to the acyl chloride (*ca.* 10.3 mmol) dissolved in *ca.* 4 mL of THF at 0 °C with stirring. The solution was then stirred for a further 2 h at room temperature. The solvent was removed under reduced pressure, leaving a yellow-brown oily residue. This was extracted with CH_2Cl_2 (2 × 30 mL) and centrifuged for *ca.* 10 min. The solvent was removed from the liquid portion under reduced pressure to give a yellow oily residue. This was dissolved in a minimum of hexane, transferred to a deactivated alumina column (1.5 × 14 cm), and eluted with hexane. A yellow band containing $[Mn_2(CO)_{10}]$ was eluted first, followed immediately by a second, virtually colorless band. The solvent was removed from the second band under reduced pressure to give a pale yellow crystalline solid which was recrystallized from hexane at −78 °C.

(b) (i) General Synthetic Route to the Compounds $[Mn(R)(CO)_5]$ (R = C_2H_5 to *n*-C_9H_{19}, *n*-$C_{11}H_{23}$, *n*-$C_{13}H_{27}$, *n*-$C_{15}H_{31}$, *n*-$C_{17}H_{35}$). $[Mn(COR)(CO)_5]$ (0.70 g) was dissolved in hexane (20 mL) and the solution refluxed for 1 h under N_2. The solvent was then removed under reduced pressure to give the product as a yellow oil. This was dissolved in a minimum of hexane, transferred to a deactivated alumina chromatography column (1.5 cm × 9 cm), and eluted with hexane. Two overlapping yellow bands were eluted, which were collected as two separate fractions. The first, bright yellow fraction contained $[Mn_2(CO)_{10}]$, and the second, pale yellow fraction contained only the product, from which the solvent was removed under reduced pressure to give a yellow oil. The products were recrystallized from hexane at −78 °C. Most of these products are yellow oils at room temperature.

(ii) General Synthetic Route to the Compounds $[Mn(R)(CO)_5]$ (R = *n*-$C_{10}H_{21}$, *n*-$C_{12}H_{25}$, *n*-$C_{14}H_{29}$, *n*-$C_{16}H_{33}$, *n*-$C_{18}H_{37}$). A solution of $Na[Mn(CO)_5]$ (3.84 mmol) prepared by reductive cleavage of $[Mn_2(CO)_{10}]$ over Na/Hg in THF (20 mL) was added dropwise over *ca.* 10 min to the alkyl bromide (*ca.* 3.84 mmol) dissolved in *ca.* 4 mL of THF at 0 °C with stirring. The solution was then stirred for 5–7 days at room temperature. The solvent was removed under reduced pressure, leaving a yellow-brown oily residue. This was extracted with CH_2Cl_2 (2 × 20 mL) and centrifuged for *ca.* 10 min. The solvent was removed from the liquid portion under reduced pressure to give a yellow-brown oil which was then purified in a manner analogous to that described in part i above. Owing to its high volatility, methylmanganese pentacarbonyl, $[Mn(CH_3)(CO)_5]$, was synthesized by a different procedure as outlined in the literature.[57]

(c) Decarbonylation of $[Mn(COR)(CO)_5]$: Kinetic Studies. The method outlined by Cotton and co-workers[36,53] was employed for these kinetic measurements. Kinetic data (obtained in duplicate) for the decarbonylation process were obtained by monitoring the decrease in intensity of the highest energy (A_1) carbonyl vibration (*ca.* 2112 cm^{-1}). A Schlenk tube containing 10 mL of hexane was placed in a constant-

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[57] King, R. B. In *Organometallic Synthesis*; Eisch, J. J., King, R. B., Eds.; Academic Press: New York, 1965; p 147.

temperature bath at 55.5 °C, and the manganese pentacarbonyl acyl complex (typically, sufficient complex to give a 0.04 M solution) was added. Aliquots were then removed periodically, and the infrared transmission was measured using the attached ordinate data processing facility. The reaction mixture was kept under nitrogen for the duration of the experiment and was degassed periodically (every 3 min) in order to prevent CO buildup. The temperature remained constant to within 0.5 °C. A plot of $\ln(I_\infty - I_t)$ versus time yielded k, the rate constant for the decarbonylation reaction (I_∞ = intensity at time ∞, I_t = intensity at time t). The results were analyzed over *ca.* 75% of the reaction by linear regression using a Casio FX702P calculator. Reactions were followed for approximately 3 half-lives, although linearity was observed over only 2 half-lives. At least 10 data points were obtained for each reaction. Results are given in Table 3.

(d) Reaction of [Mn(R)(CO)$_5$] with Triphenylphosphine: Kinetic Studies. The method outlined by Cotton and co-workers[36,53] was again employed for these kinetic measurements. Kinetic data (obtained in duplicate) for the CO insertion (alkyl migration) process were obtained by monitoring the decrease in intensity of the highest energy (A_1) carbonyl vibration (*ca.* 2105 cm^{-1}). A solution of the manganese alkyl complex in hexane (10 mL of a *ca.* 0.07 M solution) was placed in a Schlenk tube in a constant-temperature bath at 32.0 °C. An infrared spectrum was run, corresponding to time 0. The triphenylphosphine (typically, a 9 molar equiv excess) was then added to the solution in the Schlenk tube. Time 0 was taken at the time point when half of the PPh$_3$ had been added. Aliquots were then removed periodically, and the infrared transmission was measured using the attached ordinate data processing facility. The reaction mixture was kept under nitrogen for the duration of the experiment. The temperature remained constant to within 0.5 °C. A plot of $\ln(I_\infty - I_t)$ versus time yielded k_{obs}, the observed rate constant for the CO insertion process. The results were analyzed over *ca.* 75% of the reaction by linear regression using a Casio FX702P calculator. Reactions were followed for approximately 3 half-lives, although linearity was observed over only 2 half-lives. At least 10 data points were obtained for each reaction. Results are given in Table 4.

The products of the reaction all adopted a *cis* geometry and were characterized by IR, ^{1}H NMR, melting point, and elemental analysis. (As a result of the reactions being performed on very small amounts of alkyl complex, the products from all of the reactions were not fully characterized.) Typically, for *cis*-[Mn{CO(CH$_2$)$_8$CH$_3$}(CO)$_4$(PPh$_3$)]: IR (ν(CO) in CHCl$_3$) 2070 (mw), 1966 (vs, br), 1611 cm^{-1} (w); ^{1}H NMR (CDCl$_3$) δ 0.94 (3H, CH_3), 1.29 (12 H, (CH_2)$_6$CH$_3$), 1.57 (2 H, MnCOCH$_2$CH_2), 2.18 (2H, MnCOCH_2); mp 76–79 °C. Anal. Calcd for $C_{32}H_{31}MnO_5P$: C, 63.5; H, 6.25. Found: C, 62.6; H, 5.8. For *cis*-[Mn{CO(CH$_2$)$_{14}$CH$_3$}(CO)$_4$(PPh$_3$)]: IR (ν(CO) in CHCl$_3$) 2069 (mw), 1964 (vs, br), 1618 cm^{-1} (w); ^{1}H NMR (CDCl$_3$) δ 0.95 (3H, CH$_3$), 1.32 (24H, (CH_2)$_{12}$CH$_3$), 1.60 (2H, MnCOCH$_2$CH_2), 2.17 (2H, MnCOCH_2); mp 89–91 °C. Anal. Calcd for $C_{38}H_{43}MnO_5P$: C, 68.6; H, 6.5. Found: C, 67.5; H, 6.0.

Acknowledgment. We thank the University of Cape Town and the FRD for financial support.

Supplementary Material Available: Tables of IR, ^{1}H and ^{13}C NMR, and mass spectral data and a sample of experimental data and a plot of $\ln(I_\infty - I_t)$ vs t (11 pages). Ordering information is given on any current masthead page.

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