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THE SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF THE BINUCLEAR COMPLEXES $[(OC)_5MC(O)(CH_2)_nC(O)M(CO)_5]$ (M = Mn, Re; $n = 4$–8, 10) and $[(OC)_5M(CH_2)_nM(CO)_5]$ (M = Mn, Re; $n = 4$–8, 10 and M = Re, $n = 9$)

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Abstract—The $\mu(1,n)$-alkanediyl complexes $[(OC)_5M(CH_2)_nM(CO)_5]$ (M = Mn, Re; $n = 4$–8, 10) have been synthesized from the μ-diacyl compounds $[(OC)_5MC(O)(CH_2)_nC(O)M(CO)_5]$ by thermal decarbonylation. $[(OC)_5Re(CH_2)_9Re(CO)_5]$ was prepared by the reaction of $Na[Re(CO)_5]$ with 1,9-dibromononane. Some reactivity studies are reported. The effects of changing the length of the alkanediyl chain and the metal from Mn to Re are discussed. The results of this study are compared with known properties and reactions of mononuclear alkyl and acyl compounds of the type $[M(R)(CO)_5]$ and $[M(COR)(CO)_5]$ (M = Mn, Re). Rates of decarbonylation and carbonylation of some of the complexes have been measured and discussed.

The reaction in eq. (1) of the alkyl compounds $[Mn(R)(CO)_5]$

$$[Mn(R)(CO)_5] + L \longrightarrow [Mn(COR)(CO)_4(L)] \quad (1)$$

with ligands, L, where L = CO or PR'_3, is a classic example of the migratory CO insertion reaction[1,2] and continues to receive considerable interest.[3–6] This is in part due to its industrial importance, since it is a fundamental process which is crucial to many catalytic reactions.

For binuclear metal alkyl complexes, such reactions are not necessarily predictable since there is no corresponding library of fundamental processes on which to model transformations at complexes with more than one metal centre. It may well be that the same fundamental processes detailed for mononuclear systems will hold for bi- or polynuclear metal complexes either acting in parallel at each metal centre or in series at separate metal centres. A more exciting possibility is that new primary processes, pertaining only to bi- or polynuclear metal systems, are required adequately to explain the observed transformations. Thus a hydrocarbyl ligand bridging two metals may undergo a rearrangement that is not possible for a mononuclear metal complex.[7,8]

Binuclear alkanediyl complexes may also be useful models for hydrocarbons bound to metal catalyst surfaces in important catalytic reactions such as alkene polymerization and the Fischer–Tropsch reaction. They may also serve as precursors for the synthesis of bifunctional organic compounds.

We are particularly interested in trying to determine the factors that can affect the reactivity of complexes of the type $[L_mM(CH_2)_nML_m]$ where L_mM is a metal with its associated ligands. A particular class of compounds of this type is the metal pentacarbonyl alkanediyl compounds $[(OC)_5M(CH_2)_nM(CO)_5]$. Here there is the opportunity to vary the metal (M) and the length of the polymethylene chain (n) and to see what effect changing these parameters has on the reactivity of the com-

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plexes. We have previously reported the synthesis and reactivity of the complexes $[M(R)(CO)_5]$ and $[M(COR)(CO)_5]$ ($M = Mn$, Re; $R = CH_3$ to n-$C_{18}H_{37}$).[5,6,9] We now report our results on the synthesis and reactivity of the alkanediyl bridged binuclear complexes $[(OC)_5M(CH_2)_nM(CO)_5]$ ($M = Mn$, Re; $n = 4$–8, 10 and $M = Re$; $n = 9$) and $[(OC)_5MC(O)(CH_2)_nC(O)M(CO)_5]$ ($M = Mn$, Re; $n = 4$–8, 10).

EXPERIMENTAL

All reactions were carried out in Schlenk tubes under nitrogen. The compounds $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$ were purchased from Strem Chemicals U.S.A., the diacyl chlorides purchased from Aldrich, 1,9-dibromononane purchased from Aldrich and PPh_3 purchased from Merck, and were used without further purification. Tetrahydrofuran and hexane were distilled over sodium wire under nitrogen and toluene was distilled over $CaCl_2$ under nitrogen.

Infrared spectra were recorded on a Perkin–Elmer 983 spectrophotometer and ^1H and ^{13}C NMR spectra on a Varian XR 200 spectrometer using tetramethylsilane as a standard (δ 0.00 ppm). The low-resolution electron-impact mass spectra were measured on a VG Micromass 16F spectrometer at 70 eV (1.12×10^{-17} J) with an accelerating voltage of 4 kV. Melting points were determined on a Kofler hot-stage microscope (Reichert-Thermovar) and are uncorrected. Microanalyses were performed in the microanalytical laboratory at the University of Cape Town.

Synthesis of $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ ($n = 4$–8, 10): *general procedure*

The compound $[Mn_2(CO)_{10}]$ (2.00 g; 5.13 mmol) in tetrahydrofuran (THF) (30 cm^3) was stirred over a sodium amalgam (0.4 g Na in 4 cm^3 Hg) for 2 h at room temperature. The resulting solution of $Na[Mn(CO)_5]$ (10.26 mmol) was then transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the diacyl chloride, $ClC(O)(CH_2)_nC(O)Cl$ (5.13 mmol). The reaction mixture was stirred for 4.5 h at room temperature. The solvent was removed under reduced pressure, leaving a yellow oily residue which was extracted with warm chloroform (*ca* 40 cm^3) and filtered. The filtrate was reduced to *ca* 10 cm^3 and hexane was added until the solution went cloudy. Cooling to −15°C resulted in crystallization of the diacyl compounds. The yields and characterization data are given in Tables 1–4.

Synthesis of the μ-alkanediyl complexes $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ ($n = 4$–8, 10): *general procedure*

The diacyl compounds $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ ($n = 4$–8, 10) were converted into the corresponding $\mu(1,n)$-alkanediyl compounds by thermal decarbonylation. Typically, *ca* 1.00 g of $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ was dissolved in hexane (100 cm^3) and the solution was refluxed for 45 min under nitrogen. The reaction can be followed by IR spectroscopy by monitoring the disappearance of the acyl band at *ca* 1625 cm^{-1}. Removal of the hexane under reduced pressure left a creamy coloured solid which was recrystallized by dissolving in a minimum of warm chloroform and adding hexane. Cooling to −15°C resulted in the formation of the product as an off-white crystalline solid. The yields and characterization data are given in Tables 5–8.

Synthesis of $[(OC)_5ReC(O)(CH_2)_nC(O)Re(CO)_5]$ ($n = 4$–8, 10): *general procedure*

The compound $[Re_2(CO)_{10}]$ (1.20 g; 1.84 mmol) in THF (25 cm^3) was stirred over a sodium amalgam (0.3 g Na in 4 ml Hg) for 2 h at room temperature. The resulting orange solution of $Na[Re(CO)_5]$ (3.68 mmol) was transferred dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing the diacyl chloride, $ClC(O)(CH_2)_nC(O)Cl$ (1.84 mmol). The solution went cloudy almost immediately with a precipitate forming. The reaction mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure, leaving a creamy coloured residue which was extracted with warm CH_2Cl_2 (2×25 cm^3) and centrifuged at maximum speed for *ca* 10 min. The solvent was removed from the liquid portion under reduced pressure to give a creamy coloured solid which was recrystallized from warm acetone at −15°C. The yields and characterization data are given in Tables 1–4.

Synthesis of $[(OC)_5Re(CH_2)_nRe(CO)_5]$ ($n = 4$–8, 10): *general procedure*

$[(OC)_5ReC(O)(CH_2)_nC(O)Re(CO)_5]$ (0.8 g) was dissolved in toluene (80 cm^3) and the solution was refluxed for 4 h under nitrogen. The solution was filtered while hot and the filtrate reduced to *ca* 20 cm^3. This was then cooled to −15°C, resulting in the formation of off-white crystals which were fil-

Table 1. Data for $[(OC)_5MC(O)(CH_2)_nC(O)M(CO)_5]$

n	M	Yield (%)	M.p. (°C)	IR ν(CO) (cm^{-1})[a]	Elemental analysis C; found (calc.)	Elemental analysis H; found (calc.)
4	Mn	86	119–224[b]	2114w, 2050sh, 2014s, 1636w	38.5 (38.3)	1.6 (1.6)
5	Mn	82	129–132	2114w, 2050sh, 2015s, 1638w	39.1 (39.6)	2.0 (1.9)
6	Mn	78	97–99	2115w, 2052sh, 2014s, 1636w	40.6 (40.9)	2.3 (2.3)
7	Mn	60	100–104[b]	2116w, 2050sh, 2013s, 1638w	41.7 (41.9)	2.3 (2.6)
8	Mn	62	96–97	2114w, 2052sh, 2014s, 1640w	43.0 (43.0)	3.0 (2.9)
10	Mn	49	85–87	2112w, 2050sh, 2012s, 1638w	45.3 (45.1)	3.2 (3.4)
4	Re	48	144–147	2132w, 2062mw, 2021sbr, 1605w	25.1 (25.1)	1.0 (1.1)
5	Re	46	117–120	2132w, 2062mw, 2021sbr, 1605w	26.4 (26.2)	1.4 (1.3)
6	Re	52	129–132	2132w, 2062mw, 2021sbr, 1605w	27.3 (27.3)	1.6 (1.5)
7	Re	53	96–104	2132w, 2062mw, 2020sbr, 1605w	28.5 (28.3)	1.9 (1.7)
8	Re	58	122–125	2132w, 2062mw, 2014sbr, 1605w	29.1 (29.3)	1.9 (2.0)
10	Re	50	106–110	2132w, 2062mw, 2019sbr, 1605w	31.3 (31.7)	2.3 (2.4)

[a] In $CHCl_3$, w = weak, sh = shoulder, s = strong, mw = medium/weak, sbr = strong/broad.
[b] Decomposed.

Table 2. ^1H NMR data for $[(OC)_5MC(O)(CH_2)_nC(O)M(CO)_5]$[a]

n	M	$MCOCH_2$	$MCOCH_2CH_2$	$MCOCH_2CH_2(CH_2)_x$
4	Mn	2.91 tr (4H)	1.44 tr (4H)	
5	Mn	2.86 tr (4H)	1.41 bs (4H)	1.18 bs (2H)
6	Mn	2.88 bs (4H)	1.42 bs (4H)	1.20 bs (4H)
7	Mn	2.91 bs (4H)	1.47 bs (4H)	1.23 bs (6H)
8	Mn	2.90 tr (4H)	1.47 bs (4H)	1.22 bs (8H)
10	Mn	2.82 bs (4H)		1.18 bs (16H)
4	Re	2.69 tr	1.40 tr	
5	Re	2.69 tr	1.43 tr	1.23 c (2H)
6	Re	2.69 tr	1.44 c	1.22 c (4H)
7	Re	2.68 tr	1.43 c	1.22 c (6H)
8	Re	2.69 tr	1.44 c	1.22 c (8H)
10	Re	2.69 tr	1.43 c	1.22 c (12H)

[a] In $CDCl_3$ relative to TMS ($\delta = 0.00$ ppm), bs = broad singlet, tr = triplet, c = complex signal.

tered off to give the product. Yields and characterization data are given in Tables 5–8.

Synthesis of $[(OC)_5Re(CH_2)_9Re(CO)_5]$

$[Re_2(CO)_{10}]$ (1.0 g; 1.53 mmol) was stirred over a sodium amalgam (0.2 g Na in 3 cm^3 Hg) for 2 h at room temperature. The resulting orange solution of $Na[Re(CO)_5]$ (3.06 mmol) was added dropwise by syringe with rapid stirring to a Schlenk tube at 0°C containing 1,9-dibromononane (0.44 g; 1.54 mmol). The solution rapidly went cloudy with a precipitate forming. The reaction mixture was stirred for 8 h at room temperature and then the solvent was removed under reduced pressure to give a pale yellow residue. This was extracted with CH_2Cl_2 (2×20 cm^3) and centrifuged at maximum speed for *ca* 10 min. The solvent was removed from the liquid portion under reduced pressure to give a pale yellow solid. The yield and characterization data are given in Tables 5–8.

Decarbonylation of $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ (n = 7, 10): *kinetic studies*

The method outlined by Cotton and co-workers[10,11] was employed for these kinetic measurements. Kinetic data for the decarbonylation process were obtained by monitoring the decrease in intensity of the highest energy (A_1)

Table 3. ^{13}C NMR data for $[(OC)_5MC(O)(CH_2)_nC(O)M(CO)_5]$[a]

n	M	CO[b] (terminal)	ReCO (acyl)	ReCO (*cis*)[d]	ReCO (*trans*)[d]	$MCO\underline{C}H_2$ (α)	C_2 (β)	C_3 (γ)	C_4 (δ)	C_5 (ε)
4	Mn	213				66.83	23.61			
5	Mn	209				66.94	24.10	28.10		
6	Mn	209				67.13	24.15	28.64		
7	Mn	210				67.21	24.22	28.60	29.10	
8	Mn	209				67.25	24.27	28.73	29.11	
10	Mn	209				67.24	24.27	{28.54		29.25}[c]
4	Re		248.1	183.2	181.6	70.4	23.0			
5	Re		247.7	183.2	181.2	70.5	23.5	28.2		
6	Re		247.0	183.3	181.2	70.6	23.5	28.8		
7	Re		247.7	183.3	181.2	70.7	23.5	28.6	29.3	
8	Re		247.2	183.3	181.2	70.7	23.6	28.8	29.2	
10	Re		247.2	183.3	181.2	70.7	23.6	28.8	29.2	29.3

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

[b] Broad, weak signal.

[c] Peaks for these carbon atoms were not resolved or assigned.

[d] Relative to the alkyl chain.

Table 4a. Mass spectral data for $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$

Possible assignments	Relative peak intensities[b] $n = 4$	5	6	7	8	10
Parent, M	0	0	0	0	0	0
M-Mn(CO)$_5$(= M′)	15	5	5	12	4	11
M′-CO	11	6	0	0	0	0
M′-2CO	70	10	10	22	10	7
M′-3CO	70	12	32	12	7	10
M′-4CO	54[c]	30	51	31	21	8
M′-5CO	32	17	37[c]	52	92	13
M′-6CO	57	36	36	41	58[c]	44
M′-7CO	30[c]	22	20	38	60	75[c]
M′-7CO-Mn	100	16	22[c]	11	7	4
M′-2CO-CH_2	0	55	0	0	0	0
M′-3CO-CH_2	0	58	0	0	0	0
M′-4CO-CH_2	0	66[c]	0	0	0	0
M′-5CO-CH_2	0	24	0	0	0	0
M′-6CO-CH_2	0	17	12	0	0	0
M′-7CO-CH_2	6	23[c]	8	6	0	0
M′-7CO-C_2H_4	23[c]	27	18[c]	9	34	12
M′-7CO-C_3H_6	18	21[c]	10	18[c]	0	9
M′-7CO-C_4H_8	100	6	8[c]	28	36[c]	13
M′-7CO-C_5H_{10}	—	100	100	18[c]	13[c]	7
M′-7CO-C_6H_{12}	—	—	78	22	7	12[c]
M′-7CO-C_7H_{14}	—	—	—	61	23	7
M′-7CO-C_8H_{16}	—	—	—	—	100	18[c]
M′-7CO-C_9H_{18}	—	—	—	—	—	8
M′-7CO-$C_{10}H_{20}$	—	—	—	—	—	64

[a] All ions have a single positive charge.

[b] Peak intensities relative to base peak at *m*/*z* 28 ($[CO]^+$).

[c] These assignments may be ambiguous.

Table 4b. Mass spectral data for $[(OC)_5ReC(O)(CH_2)_nC(O)Re(CO)_5]^a$

Possible assignments[a]	Relative peak intensities[b] $n = 4$	5	6	7	8	10
M	0	0	0	0	0	0
M-5CO = M′	12	14	21	18	10	8
M′-CO	18	9	7	10	12	9
M′-2CO	7	20	11	18	16	14
M′-3CO	17	24	10	10	10	13
M′-4CO	12	10	9	8	15	21
M′-5CO	24	21	13	14	10	17
M′-6CO	31	8	10	12	17	12
M′-7CO	11	16	13	15	12	19
M′-2CO-$(CH_2)_n$-Re	28	32	23	41	46	34
M′-7CO-C_2H_4	12	4	4	8	0	9
M′-7CO-C_3H_6	0	0	3	0	0	7
M′-7CO-C_4H_8	14	9	0	0	10	3
M′-7CO-C_5H_{10}	—	21	0	6	7	0
M′-7CO-C_6H_{12}	—	—	18	4	0	4
M′-7CO-C_7H_{14}	—	—	—	16	3	8
M′-7CO-C_8H_{16}	—	—	—	—	20	10
M′-7CO-C_9H_{18}	—	—	—	—	—	0
M′-7CO-$C_{10}H_{20}$	—	—	—	—	—	24
[Re]	100	100	100	100	68	100
[CO]	82	23	42	100	100	29

[a] Peaks due to $[Re(CO)_n]$ (n = 2–6) were seen in all of these mass spectra.

[b] All ions have a single positive charge.

[c] Peak intensities relative to base peak for $[Re]^+$ or $[CO]^+$.

[d] Intensity given is that of the most abundant isotope distribution.

Table 5. Data for $[(OC)_5M(CH_2)_nM(CO)_5]$

n	M	Yield (%)	M.p. (°C)	IR ν(CO) (cm^{-1})[a]	Elemental analysis C; found (calc.)	H; found (calc.)
4	Mn	86	136–139 (decomp.)	2104 (w), 2007 (vs)	37.6 (37.7)	1.8 (1.8)
5	Mn	80	123–126	2104 (w), 2007 (vs)	39.0 (39.2)	2.3 (2.2)
6	Mn	74	120–128	2105 (w), 2007 (vs)	40.8 (40.5)	2.7 (2.6)
7	Mn	51	69–72	2105 (w), 2007 (vs)	41.1 (41.8)	2.6 (2.9)
8	Mn	78	71–74	2104 (w), 2007 (vs)	43.1 (43.0)	3.2 (3.2)
10	Mn	69	66–69	2104 (w), 2007 (vs)	45.1 (45.3)	3.7 (3.8)
4	Re	42	170–172	2122 (mw), 2010 (s), 1977 (m)	23.8 (23.7)	1.0 (1.1)
5	Re	58	141–143	2123 (mw), 2008 (s), 1977 (m)	24.9 (24.9)	1.3 (1.4)
6	Re	62	162–164	2122 (mw), 2009 (s), 1978 (m)	25.8 (26.1)	1.3 (1.6)
7	Re	69	122–127	2122 (mw), 2008 (s), 1977 (m)	27.1 (27.2)	1.9 (1.9)
8	Re	54	151–155	2122 (mw), 2008 (s), 1978 (m)	28.1 (28.3)	2.0 (2.1)
9	Re	40	104–106	2123 (mw), 2007 (s), 1978 (m)	29.0 (29.3)	1.9 (2.3)
10	Re	71	138–140	2122 (mw), 2007 (s), 1978 (m)	30.1 (30.3)	2.2 (2.5)

[a] In $CHCl_3$; mw = medium weak, s = strong, m = medium, w = weak, vs = very strong.

Table 6. ^1H NMR data for $[(OC)_5M(CH_2)_nM(CO)_5]$[a]

n	M	MCH_2	MCH_2CH_2	Central $(CH_2)_x$
4	Mn	1.08 (br,4H)	1.72 (br,4H)	
5	Mn	1.09 (br,4H)	1.66 (br,6H)	
6	Mn	1.12 (br,4H)	1.45 (br,8H)	
7	Mn	1.06 (br,4H)	1.68 (br,4H)	1.35 (br,6H)
8	Mn	1.05 (br,4H)	1.68 (br,4H)	1.34 (br,8H)
10	Mn	1.05 (br,4H)	1.69 (br,4H)	1.37 (br,12H)
4	Re	1.01 (tr,4H)	1.78 (br,4H)	
5	Re	0.98 (tr,4H)	1.76 (br,4H)	1.30 (brs,2H)
6	Re	0.91 (tr,4H)	1.70 (br,4H)	1.26 (brs,4H)
7	Re	0.96 (tr,4H)	1.76 (br,4H)	1.28 (brs,6H)
8	Re	0.99 (tr,4H)	1.77 (br,4H)	1.27 (brs,8H)
9	Re	0.96 (tr,4H)	1.78 (br,4H)	1.27 (brs,10H)
10	Re	0.96 (tr,4H)	1.77 (br,4H)	1.27 (brs,12H)

[a] In $CDCl_3$ relative to TMS ($\delta = 0.00$ ppm), tr = triplet, br = broad signal, brs = broad singlet.

Table 7. ^{13}C NMR data for $[(OC)_5M(CH_2)_nM(CO)_5]$[a]

n	M	Mn(CO)[b] (terminal)	ReCO (*cis*)[c]	ReCO (*trans*)[c]	$MnCH_2$ (α)	C_2	C_3	C_4	C_5
4	Mn	214			6.2	43.3			
5	Mn	215			6.6	36.7	41.2		
6	Mn	213			6.9	35.1	37.4		
7	Mn	213			7.0	37.7	35.5	29.3	
8	Mn	214			7.1	37.3	35.6	29.2	
10	Mn	214			7.1	37.3	35.7	29.7	29.2
4	Re		186.1	181.4	−9.5	49.9			
5	Re		186.1	181.4	−9.2	40.3	37.8[d]		
6	Re		186.0	181.5	−9.1	39.1	37.1		
7	Re		186.1	181.5	−9.1	39.2	37.3	29.6[d]	
8	Re		186.0	181.5	−9.1	39.1	37.5	29.7	
9	Re		186.0	181.5	−9.1	39.2	37.4	29.2	29.8[d]
10	Re		186.0	181.5	−9.0	39.2	37.5	29.1	29.8

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

[b] Broad, weak signal.

[c] Relative to the alkyl chain.

[d] Assignments were made on the basis of relative intensities.

carbonyl vibration (*ca* 2114 cm^{-1}). A Schlenk tube containing 10 cm^3 hexane was placed in a constant temperature bath at 55.5°C, at which point the temperature dropped slightly. When the temperature had reached 55.5°C again, the manganese acyl complex (typically sufficient complex to give a 0.04 M solution) was added. Aliquots were then removed periodically and the infrared transmission measured using the attached ordinate data processing facility. The reaction was kept under nitrogen for the duration of the experiment and was degassed periodically, by a flow of nitrogen, in order to prevent CO build up. The temperature remained constant to within 0.5°C. A plot of ln (I_∞-I_t) vs time

Table 8a. Mass spectral data for $[(OC)_5Mn(CH_2)_nMn(CO)_5]$[a]

Possible assignments[b]	Relative peak intensities[c]					
	$n = 4$	5	6	7	8	10
M	3	0	2	0	0	0
M-CO	2	2	0	0	0	0
M-2CO	4	0	0	0	0	0
M-3CO	0	3	1	6	12	0
M-4CO	6	0	10	18	18	35
M-5CO	10	7	6	22	26	19
M-6CO	5	4	0	6	9	7
M-7CO	4	4	8	11	10	6
M-8CO	11	8	6	10	13	13
M-9CO	28	19	21	44	43	20
M-10CO	21	10	18	16	20	28
M-10CO-Mn	0	12	10	20	22	39
M-Mn$(CO)_5$	8	0	10	5	11	16
M-CO-$(CH_2)_n$	0	0	10	0	26	7
M-2CO-$(CH_2)_n$	6	2	6	0	9	6
M-3CO-$(CH_2)_n$	10	1	0	2	10	13
M-4CO-$(CH_2)_n$	5	0	8	3	13	20
M-5CO-$(CH_2)_n$	4	20	6	2	43	28
M-6CO-$(CH_2)_n$	11	18	21	5	20	36
M-7CO-$(CH_2)_n$	28	12	18	10	0	60
M-8CO-$(CH_2)_n$	21	4	8	6	23	6
M-9CO-$(CH_2)_n$	6	10	22	14	5	11
M-10CO-$(CH_2)_n$	27	14	41	8	36	22
M-10CO-$(CH_2)_n$-Mn	100	100	100	100	100	100

[a] All spectra exhibited most of the peaks characteristic of $[Mn(R)(CO)_5]$ species, namely $[Mn(CO)_5]^+$, $[Mn(CO)_4]^+$, $[Mn(CO)_3]^+$, $[Mn(CO)]^+$, $[Mn(H)]^+$, $[Mn]^+$ and $[CO]^+$.

[b] All ions have a single positive charge.

[c] Peak intensities relative to base peak at m/z 55 (Mn).

yielded k_{OBS} (I_∞ = intensity at time = ∞ ; I_t = intensity at time = t). Reactions were followed for approximately three half-lives. Results are given in Table 9.

Reaction of $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ ($n = 8, 10$) *with* PPh_3: *kinetic studies*

The method outlined by Cotton and coworkers[10,11] was again employed for these kinetic measurements. Kinetic data for the alkyl migration process were obtained by monitoring the decrease in intensity of the highest energy (A_1) carbonyl vibration (*ca* 2104 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°C. An infrared spectrum was run, corresponding to time = 0. The triphenylphosphine (typically, an 18-molar excess) was then added to the solution in the Schlenk tube. Time = 0 was taken at the point when half of the PPh_3 had been added. Aliquots were then removed periodically and the infrared transmission measured using the attached ordinate data processing facility. The reaction was kept under nitrogen for the duration of the experiment. The temperature remained constant to within 0.5°C. A plot of ln (I_∞-I_t) *vs* time yielded K_{OBS}. Reactions were followed for approximately three half-lives. Results are given in Table 10.

RESULTS AND DISCUSSION

The binuclear and acyl compounds $[(OC)_5MnC(O)(CH_2)_4C(O)Mn(CO)_5]$[12,13], $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ ($n = 5, 6$)[14] and $[(OC)_5MnC(O)(CH_2)_8C(O)Mn(CO)_5]$[15] have previously been reported. We now report some further characterization data for these compounds and the synthesis of the new compounds $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ ($n = 7, 10$). These compounds were all prepared by the reaction of

Table 8b. Mass spectral data for $[(OC)_5Re(CH_2)_nRe(CO)_5]$

Possible	Relative peak intensities[b]						
assignments[a]	$n = 4$	5	6	7	8	9	10
M	8	4	6	10	3	12	4
M-CO	5	10	0	12	4	6	0
M-2CO	0	7	9	0	12	8	0
M-3CO	10	12	7	9	0	0	5
M-4CO	10	0	6	4	8	9	6
M-5CO	28	12	18	22	14	17	28
M-6CO	24	22	17	14	21	27	20
M-7CO	30	32	21	14	35	28	20
M-8CO	32	14	18	31	27	26	22
M-9CO	24	28	22	24	24	23	14
M-10CO	28	30	31	30	38	28	27
M-$(CH_2)_n$	0	0	7	2	8	4	8
M-CO-$(CH_2)_n$	10	4	6	3	14	8	20
M-2CO-$(CH_2)_n$	10	8	18	11	21	6	20
M-3CO-$(CH_2)_n$	28	4	17	7	35	7	22
M-4CO-$(CH_2)_n$	24	5	21	10	27	3	14
M-5CO-$(CH_2)_n$	30	8	18	10	24	12	27
M-6CO-$(CH_2)_n$	32	6	22	12	38	4	8
M-7CO-$(CH_2)_n$	24	7	31	7	20	13	12
M-8CO-$(CH_2)_n$	28	12	21	17	18	12	21
M-9CO-$(CH_2)_n$	18	10	14	18	19	17	14
M-10CO-$(CH_2)_n$	28	31	28	37	42	29	40
M-10CO-$(CH_2)_n$-Re	44	61	58	48	38	54	41
M-$(CH_2)_n$-$Re(CO)_5$	100	100	100	100	100	100	100
M-10CO-Re	20	12	21	18	14	29	20
M-$(CH_2)_n$-Re-6CO	32	41	24	48	33	31	38
M-$(CH_2)_n$-Re-7CO	30	35	54	41	27	27	36
M-$(CH_2)_n$-Re-8CO	50	28	38	23	40	43	30
M-$(CH_2)_n$-Re-9CO	42	20	21	37	22	34	31
M-$(CH_2)_n$-Re-10CO	24	28	20	20	29	20	18
M-$Re(CO)_5$	31	26	28	20	28	34	14
M-$Re(CO)_5$-CO	10	7	11	8	10	7	9
M-$Re(CO)_5$-2CO	21	18	14	16	28	10	17
M-$ReE(CO)_5$-3CO	20	21	31	26	22	18	27
M-$Re(CO)_5$-4CO	30	24	30	28	18	32	30
CO	18	14	28	22	50	14	10

[a] All ions have a single, positive charge.

[b] Peak intensities relative to base peak, i.e $[Re(CO)_5]^+$.

Table 9. Kinetic data for the decarbonylation of $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ in hexane at 55.5°C

n	k_1 ($\times 10^4$ s^{-1})	k_3 ($\times 10^4$s^{-1})	$\log k_1$	$\log k_3$	$t_{1/2(1)}$ (min)	$t_{1/2(3)}$ (min)
7	2.45	0.72	−3.61	−4.14	47.2	160.5
10	5.17	1.44	−3.29	−3.84	22.4	80.2
4[a]	1.1	—	−3.96	—	105.0	—

[a] M. Bothma, J. M. Andersen and J. R. Moss, unpublished results.

Table 10. Kinetic data for the reaction of $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ with PPh_3 at 32°C in hexane

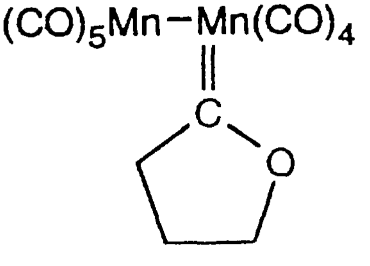
n	k_1 ($\times 10^4\ s^{-1}$)	k_3 ($\times 10^4 s^{-1}$)	$\log k_1$	$\log k_3$	$t_{1/2(1)}$ (min)	$t_{1/2(3)}$ (min)
8	1.59	—	−3.80	—	72.6	—
10	2.06	0.98	−3.69	−4.01	56.0	117.5

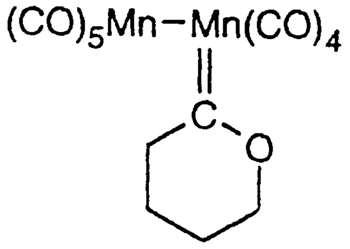
$Na[Mn(CO)_5]$ with the appropriate diacyl chloride as shown in eq (2).

$$2Na[Mn(CO)_5] + ClC(O)(CH_2)_nC(O)Cl \longrightarrow 2NaCl + [(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5] \quad (n = 4\text{–}8,\ 10). \quad (2)$$

All the compounds were isolated as cream/off-white microcrystalline solids which, like their mononuclear analogues, are stable both thermally and to air, and in solution when kept under nitrogen.[5,6]

Attempts to prepare the compounds $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ ($n = 3$ or 4) were made by King in the 1960s[16] by the reaction of $Na[Mn(CO)_5]$ with $Br(CH_2)_nBr$ or with $ClCO(CH_2)_3Cl$. The products of these reactions, however, were later shown not to be the alkanediyl compounds as originally suggested but the binuclear cyclic carbene complexes as shown below.[17–19]





The first reported synthesis of a compound of the type $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ came from Raab *et al.* in 1983[20] who reacted $[Mn(CH_3)(CO)_5]$ with Ph_3CBF_4 followed by ethylene and $Na[Mn(CO)_5]$ to give $[(OC)_5MnCH_2CH_2Mn(CO)_5]$. In 1985 Mapolie *et al.* followed with the synthesis of $[(OC)_5Mn(CH_2)_4Mn(CO)_5]$, formed by thermal decarbonylation of the acyl precursor, $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$.[21] This strategy was then extended to the synthesis of the pentanediyl and hexanediyl derivatives, $[(OC)_5Mn(CH_2)_5Mn(CO)_5]$ and $[(OC)_5Mn(CH_2)_6Mn(CO)_5]$ i.e. thermal decarbonylation of the relevant acyl precursors.[14] The most recent reports have come from Lindner *et al.* who have synthesized $[(OC)_5Mn(CH_2)_3Mn(CO)_5]$[22] and $[(OC)_5Mn(CH_2)_{10}Mn(CO)_5]$[23] from $K[Mn(CO)_5]$ and the bistriflates, $Y(CH_2)_nY$ ($Y = F_3CSO_3$; $n = 3, 10$).

We now report the synthesis and characterization of the compounds $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ ($n = 4$–8, 10). The compounds with $n = 7$ and 8 are new. All of these compounds were synthesized by thermal decarbonylation of the acyl precursors, as shown in eq. (3)

$$[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5] \xrightarrow[\text{reflux}]{\text{hexane}} 2CO + [(OC)_5Mn(CH_2)_nMn(CO)_5] \quad (n = 4\text{–}8,\ 10). \quad (3)$$

These binuclear compounds appear to be much more stable than their mononuclear analogues, especially the $[(OC)_5MnCH_2CH_2Mn(CO)_5]$[22] and $[(OC)_5MnCH_2CH_2CH_2Mn(CO)_5]$[23] species, even though they contain β-hydrogen atoms. This increased stability is presumably as a result of the second manganesepentacarbonyl moiety exerting a stabilizing effect. This supports the premise that ethyl and n-propyl manganesepentacarbonyl are unstable due to a reason other than β-elimination, i.e. a very rapid alkyl migration (carbonylation) reaction.[6] The $\text{-}(CH_2)_nMn(CO)_5$ moiety may be expected not to undergo alkyl migration nearly as easily as a -$(CH_2)_nH$ group as a result of size and electronic effects.

While relatively few compounds of the type $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ and $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ are known, the list is even shorter for rhenium. The only binuclear acyl compound known is the butanediyl derivative, $[(OC)_5ReC(O)(CH_2)_4C(O)Re(CO)_5]$, prepared by the reaction of $Na[Re(CO)_5]$ with adipoyl chloride.[14] We now report the synthesis of this compound, with additional characterization data, and the synthesis of the new compounds $[(OC)_5ReC(O)(CH_2)_nC(O)Re(CO)_5]$ ($n = 5$–8, 10). All the compounds were prepared by the reaction of $Na[Re(CO)_5]$ with the appropriate diacyl chloride, as shown in eq. (4)

$$2Na[Re(CO)_5] + ClC(O)(CH_2)_nC(O)Cl \xrightarrow[25^\circ C]{THF} 2NaCl + [(OC)_5ReC(O)(CH_2)_nC(O)Re(CO)_5] \quad (n = 4\text{–}8,\ 10). \quad (4)$$

All the compounds were isolated as off-white microcrystalline solids which, like their mononuclear analogues,[9] are stable in air and in solution when kept under nitrogen.

Only three alkanediyl complexes of rhenium, namely $[(OC)_5Re(CH_2)_nRe(CO)_5]$ ($n = 2$–4) have previously been reported.[14,24] We now report the syntheses of the $n = 4$ compound and the compounds $[(OC)_5Re(CH_2)_nRe(CO)_5]$ ($n = 5$–10). As with the mononuclear alkyl compounds, $[Re(R)(CO)_5]$, two synthetic strategies were used.[9] The first involves the thermal decarbonylation of the acyl precursors, as shown in eq. (5), while the second procedure involves the direct reaction of $Na[Re(CO)_5]$ with a dibromoalkane, as shown in eq. (6).

$$[(OC)_5ReC(O)(CH_2)_nC(O)Re(CO)_5] \xrightarrow[110^\circ C]{toluene} 2CO + [(OC)_5Re(CH_2)_nRe(CO)_5] \quad (n = 4\text{–}8, 10) \quad (5)$$

$$2Na[Re(CO)_5] + Br(CH_2)_9Br \xrightarrow[25^\circ C]{THF} 2NaBr + [(OC)_5Re(CH_2)_9Re(CO)_5] \quad (6)$$

All of the above binuclear acyl and alkyl compounds have been fully characterized by IR, ^1H and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry. The data are listed in Tables 1–8.

The compounds $[(OC)_5MC(O)(CH_2)_nC(O)M(CO)_5]$ (M = Mn, Re; $n = 4$–8, 10)

Infrared spectra. The IR spectra in the $\nu(CO)$ region are in good agreement with those reported for $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$[12–15] and $[(OC)_5ReC(O)(CH_2)_4C(O)Re(CO)_5]$[14] and, like their mononuclear analogues,[6,9] show the expected number of peaks for $[M(COR)(CO)_5]$ species[25] (where R = -$(CH_2)_nC(O)M(CO)_5$), namely A_1 (2114 cm^{-1}, Mn; 2132 cm^{-1}, Re), B (2050 cm^{-1}, Mn; 2062 cm^{-1}, Re), E and A_1 (2013 cm^{-1}, Mn; 2021 cm^{-1}; Re) and acyl (1638 cm^{-1}, Mn; 1605 cm^{-1}, Re). There is no significant variation in $\nu(CO)$ upon changing the length of the bridging hydrocarbyl chain.

^1H *NMR Spectra.* From the ^1H NMR data, it can be seen that, as was noted for the mononuclear acyl compounds,[6,9] separate resonances are observed only for the α and β protons of the bridging alkyl chain. The remaining (central) methylene protons appear either as a broad singlet or a complex signal. There is no significant variation in chemical shift when changing the length of the alkyl chain. Thus, integration is the only way to distinguish between these compounds using ^1H NMR measurements. Assignment of the peaks was made by comparison with the spectral data reported for the mononuclear compounds $[Mn(COR)(CO)_5]$[6] and $[Re(COR)(CO)_5]$[9] and with the spectra reported for $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ ($n = 4$–6, 8)[14,15] and $[(OC)_5ReC(O)(CH_2)_4C(O)Re(CO)_5]$.[14]

^{13}C *NMR Spectra.* No ^{13}C NMR data has previously been reported for any of these compounds. Thus, assignment of the peaks was made by comparison with the mononuclear compounds $[Mn(COR)(CO)_5]$[6] and $[Re(COR)(CO)_5]$.[9] The terminal carbonyl resonances are at the expected positions and, for M = Mn, were not resolved. However, for M = Re the peaks due to the *cis* and *trans* CO groups were assigned, on the basis of relative intensities (4:1). For M = Mn, separate resonances were observed for all of the different carbons of the alkyl chain for the $n = 4$–8 compounds. For the $n = 10$ compound, the peaks due to the central methylene carbon atoms were not resolved. For M = Re, all of the carbon atoms in the bridging alkyl chain were assigned. Since all these binuclear compounds are symmetrical, some of the carbon atoms in the alkyl chain are equivalent and will resonate at identical positions, e.g. for $[(OC)_5MC(O)(CH_2)_7C(O)M(CO)_5]$ only four peaks are observed for the alkyl chain as a result of three pairs of identical carbon atoms. The central carbon atom is unique and is only half the intensity of the other peaks. When compared with the ^{13}C NMR spectra of the starting acyl halides, $ClC(O)(CH_2)_nC(O)Cl$, it can be seen that the influence of the metal atom is only really apparent in the α and β methylene positions.

Mass spectra. The mass spectra are reported in Table 4. They are all similar and relatively simple. No parent molecular ions were seen for any of the compounds; the parent ion in all cases was $[M-5CO]^+$ ($= M'$). The predominant fragmentation pathway was loss of carbonyl groups (from M') followed by sequential loss of methylene fragments.

The compounds $[(OC)_5M(CH_2)_nM(CO)_5]$ ($M =$ Mn, Re; $n = 4$–8, 10 and $M =$ Re, $n = 9$)

Infrared spectra. The infrared spectra in the $\nu(CO)$ region agree well with those reported for $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ ($n = 3$–6, 10)[14,21–23] and $[(OC)_5Re(CH_2)_nRe(CO)_5]$ ($n = 3$, 4).[14,24] They show the expected number of peaks for $[M(R)(CO)_5]$ species[25] (where $M = -(CH_2)_nM(CO)_5$), namely A_1 (2104 cm^{-1}, Mn; 2122 cm^{-1}, Re) and E and A_1 (2007 cm^{-1}, Mn; 2008 cm^{-1} and 1977 cm^{-1}, Re). There was no detectable variation in $\nu(CO)$ upon changing the length of the bridging hydrocarbyl chain.

^1H *NMR spectra.* The ^1H NMR data are reported in Table 6 and show that separate resonances are observed for the α and β protons of the bridging hydrocarbyl chain. The remaining (central) methylene protons of the $n = 7$–10 compounds resonate as a broad singlet. For $n = 5$ and 6 and $M =$ Mn, the central CH_2 protons resonate together with the β hydrogens as one broad signal. The signal for the β hydrogens in these two compounds is at slightly higher field, namely 1.66 and 1.45 ppm, than that for the other compounds (*ca* 1.69 ppm). This is presumably due to the signals for the β protons and central protons not being resolved; the central methylene protons thus cause the overall signal to be shifted slightly upfield. For $M =$ Re, separate resonances are seen for the γ protons of the $n = 5$ and $n = 6$ compounds. For all of the compounds, there is no detectable variation in chemical shift upon changing the length of the bridging hydrocarbyl chain.

^{13}C *NMR spectra.* The ^{13}C NMR data are shown in Table 7. The spectra were all similar to each other and relatively simple. The carbonyl resonances were at the expected positions and did not vary upon changing the length of the μ-hydrocarbyl group. Separate resonances are seen for all of the carbon atoms in the alkyl chain. The signals at *ca* 7 ppm for $M =$ Mn and -9.1 ppm for $M =$ Re were assigned to C_α, i.e. the carbon atom of the alkyl chain directly bonded to the metal atom. This indicates that the metal atom is exerting a strong shielding effect and the effect is greater for $M =$ Re than $M =$ Mn.

Mass spectra. The mass spectra data are given in Table 8. They are all similar and relatively simple. For $M =$ Mn and $M =$ Re, two fragmentation patterns are observed. The first is the usual successive loss of carbonyl groups. For $M =$ Mn the second pathway involves the loss of the $[Mn(CO)_5]$ moiety to form $[Mn(C_nH_{2n})(CO)_5]^+$ and for $M =$ Re it involves initial loss of the bridging alkyl group, $(CH_2)_n$, followed by successive loss of carbonyl groups.

Decarbonylation of $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ ($n = 7$, 10): *kinetic studies*

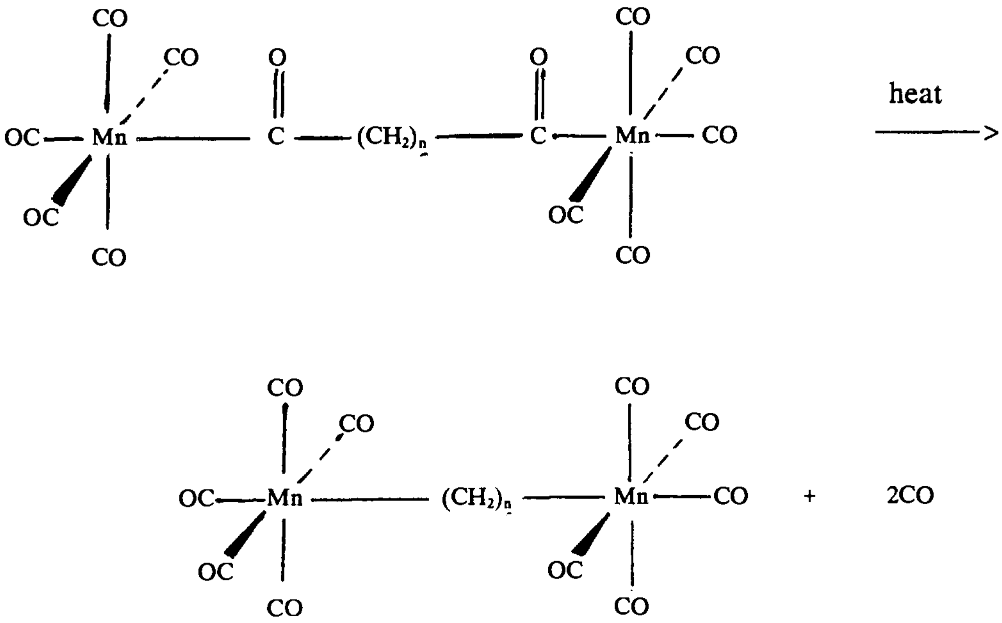
For a mononuclear acyl compound of the type $[M(COR)(CO)_5]$, the rate of decarbonylation to $[Mn(R)(CO)_5]$ is given by eq. (7)[26]

$$\frac{d[[Mn(R)(CO)_5]]}{dt} = k[[Mn(COR)(CO)_5]] \qquad (7)$$

which may hold for binuclear species. The decarbonylation reactions of $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ ($n = 7$, 10), eqn (8), were followed kinetically by the same method used for the mononuclear species, $[Mn(COR)(CO)_5]$.[6] The results are given in Table 9.

The binuclear acyl compounds $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ ($n = 4$–6, 10) are known[14,23] but the decarbonylation rate has only been investigated for $[(OC)_5MnC(O)(CH_2)_4C(O)Mn(CO)_5]$.[27] The results in Table 9 show that both the $n = 7$ and $n = 10$ compounds decarbonylate in two stages, i.e. presumably one end of the molecule decarbonylates slower than the other. This may be the result of increased steric hindrance that is encountered when the two ends of the molecule move closer together. The assumption is supported by the fact that the $n = 10$ binuclear compound decarbonylates (in both stages) approximately twice as fast as the $n = 7$ compound. The first decarbonylation step for these binuclear species is faster than the rates observed for the mononuclear analogues $[Mn(COR)(CO)_5]$[6] while the second stage is considerably slower. The $n = 4$ compound was found to decarbonylate in only one stage.[27] This may be a function of the shorter alkyl chain, which may conceivably orientate the two $[Mn(CO)_5]$ moieties in a different manner relative to each other, than in the $n = 7$ or 10 compounds.

Thus, the decarbonylation of $[(OC)_5MnC(O)$



(8)

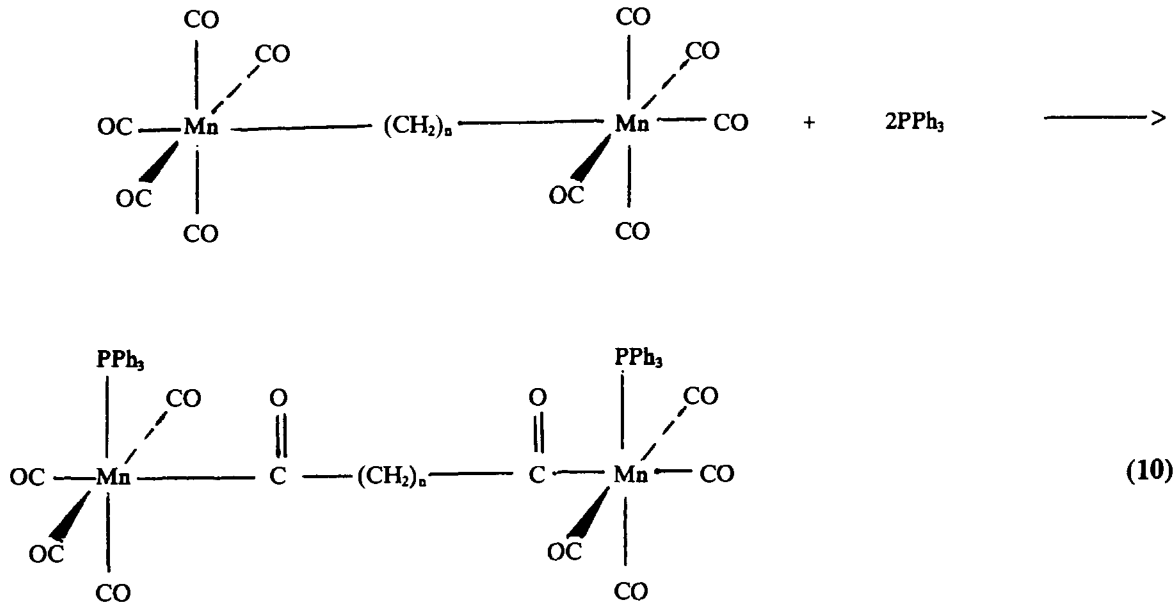
$(CH_2)_nC(O)Mn(CO)_5]$ ($n = 7$, 10) may follow the general scheme outlined in Scheme 1 (with $k_1 \gg k_3$).

Reaction of $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ ($n = 8$, 10) *with* PPh_3: *kinetic studies*

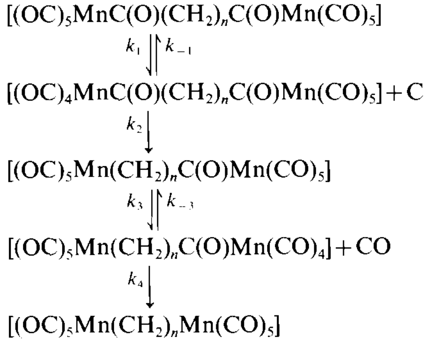
For a mononuclear alkyl compound of the type $[Mn(R)(CO)_5]$, if a large excess of incoming ligand, L, is used, the rate of alkyl migration, to form $[Mn(COR)(CO)_4(L)]$, is given by eq. 9[26] (and pseudo-first-order kinetics are observed)

$$\frac{d[[Mn(COR)(CO)_4(L)]]}{dt} = k[[Mn(R)(CO)_5)]] \qquad (9)$$

which may also hold for binuclear species. The reaction of $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ with PPh_3, as shown in eq. 10, was followed kinetically by the same method used for the mononuclear species, $[Mn(R)(CO)_5]$.[6]



(10)



Scheme 1.

The results are shown in Table 10 and show the $n = 8$ compound to react in one identifiable stage, whereas the $n = 10$ compound reacts in two stages.

CONCLUSIONS

We have synthesized and characterized several binuclear acyl and alkyl compounds of the type $[(OC)_5MC(O)(CH_2)_nC(O)M(CO)_5]$ and $[(OC)_5M(CH_2)_nM(CO)_5]$.

The rhenium compounds $[(OC)_5ReC(O)(CH_2)_nC(O)Re(CO)_5]$ take considerably longer to decarbonylate (4 h at 111°C) compared with the analogous manganese compounds $[(OC)_5MnC(O)(CH_2)_nC(O)Mn(CO)_5]$ (45 min at 69°C). This is indicative of a much stronger rhenium–carbonyl bond than manganese–carbonyl bond. This is borne out by comparing the infrared spectra of the two systems—the acyl carbonyl stretch for M = Re occurs at *ca* 1605 cm^{-1} whereas that for M = Mn occurs at *ca* 1638 cm^{-1}. This means that the C=O bond for M = Re is weaker than that for M = Mn, implying that the M—C bond is stronger for M = Re.

The stability of the shorter chain binuclear species, e.g. $-(CH_2)_4-$ is remarkable compared with their mononuclear counterparts. This refutes assumptions that the short chain mononuclear alkyl are unstable due to β hydride elimination.

The rate studies carried out indicate that the longer chain binuclear compounds undergo decarbonylation and alkyl migration reactions in two distinct stages. This is presumably as a result of the increased steric hindrance imposed by the bulky second $[Mn(CO)_5]$ moiety. For the reaction with PPh_3, the second step is considerably slower than the first, presumably as a result of both the steric and electronic effects imposed by the coordinated PPh_3.

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