Synthesis and Reactivity of the $\mu(1,n)$-Alkanediyl Complexes $[(OC)_5M(CH_2)_nM(CO)_5]$ (M = Mn, n = 4—6; M = Re, n = 3 or 4)†

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The $\mu(1,n)$-alkanediyl complexes $[(OC)_5M(CH_2)_nM(CO)_5]$ (M = Mn, n = 4—6; M = Re, n = 4) have been synthesised from the μ-diacyl compounds $[(OC)_5M(O)C(CH_2)_nC(O)M(CO)_5]$ by thermal decarbonylation. The compound $[(OC)_5Re(CH_2)_3Re(CO)_5]$ was prepared by the reaction of $Na[Re(CO)_5]$ with $Z(CH_2)_3Z$ ($Z = OSO_2CF_3$). The reactivity of the $\mu(1,n)$-alkanediyl complexes towards a variety of reagents including PR_3, CO, CO–H_2, and halogens have been investigated. 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 to known properties and reactions of mononuclear alkyl complexes $[MR(CO)_5]$ (M = Mn or Re).

The reaction (1) of the alkyl compounds $[MnR(CO)_5]$ with

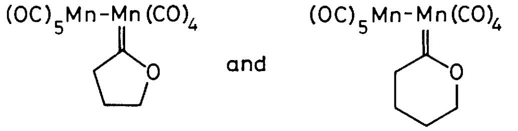
$$[MnR(CO)_5] + L \longrightarrow [Mn(CO)_4(COR)L] \quad (1)$$

ligands L, where L = CO or PR_3, R = CH_3, CH_2CH_3, *etc.*, is the classic example of the migratory CO insertion reaction[1,2] and continues to receive considerable attention.[3,4] This is in part due to its industrial importance, since it is a fundamental process which is crucial to many catalytic reactions.

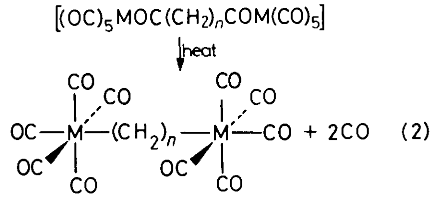
For binuclear metal alkyl complexes such reactions are not necessarily predictable since there is no corresponding library of fundamental processes with which to model transformations at complexes with more than one metal centre. It may well be that the same fundamental processes detailed for mononuclear systems will hold for bi- or poly-nuclear 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 poly-nuclear 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.[5,6] We now report on our studies of the alkanediyl complexes $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ (n = 4—6) which are close binuclear analogues of $[MnR(CO)_5]$. We also describe the analogous dirhenium compounds $[(OC)_5Re(CH_2)_nRe(CO)_5]$ (n = 3 or 4). The preparation and some reactions of $[(OC)_5Mn(CH_2)_4Mn(CO)_5]$ were briefly described in a preliminary communication.[7]

Results and Discussion

Attempts to prepare the compounds $[(OC)_5Mn(CH_2)_n$-$Mn(CO)_5]$ (n = 3 or 4) were made by King in the 1960s[8] 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.[9,10] Thus, until our work, the only $\mu(1,n)$-alkanediyl compound known of the type $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ was $[(OC)_5Mn(CH_2)_2Mn(CO)_5]$ prepared by the reaction of $Na[Mn(CO)_5]$ with $[Mn(CO)_5(C_2H_4)]^+$; the analogous dirhenium compound had been prepared in a similar way.[11]



We now report that the $\mu(1,n)$-alkanediyl compounds $[(OC)_5M(CH_2)_nM(CO)_5]$ (M = Mn, n = 4—6; M = Re, n = 4) can readily be obtained by the decarbonylation of the corresponding diacyl compounds. The decarbonylation [equation (2)] is effected by refluxing the diacyl compounds in either hexane for 15 min (for M = Mn) or in toluene (for M = Re).



(2)

	M	n
(1)	Mn	4
(2)	Mn	5
(3)	Mn	6
(4)	Re	3
(5)	Re	4

The diacyl compounds themselves are readily obtained by the reaction of the metal pentacarbonyl anion with the appropriate 1,n-diacyl chloride in tetrahydrofuran (thf) at room temperature.

$$2Na[M(CO)_5] + ClOC(CH_2)_nCOCl \longrightarrow [(OC)_5MOC(CH_2)_nCOM(CO)_5] + 2NaCl \quad (3)$$

The diacyl compound $[(OC)_5MnOC(CH_2)_4COMn(CO)_5]$ has been previously reported[12,13] but we now give additional characterisation data; the other diacyl compounds are all new. Compound (4) was prepared by reaction of $CF_3O_2SO(CH_2)_3$-OSO_2CF_3 with $Na[Re(CO)_5]$ in thf at room temperature [equation (4), Z = CF_3O_2SO]. Attempts to prepare $\mu(1,3)$-

$$2Na[Re(CO)_5] + Z(CH_2)_3Z \longrightarrow [\{Re(CO)_5\}_2\{\mu\text{-}(CH_2)_3\}] \quad (4)$$

(4)

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† *Non-S.I. unit employed:* atm = 101 325 Pa.

Table 1. Yields, m.p.s, and analytical data for compounds (**1**)—(**5**)

Compound	n[a]	M.p. (°C)	Yield (%)	Analysis[b] (%) C	Analysis[b] (%) H
(**1**)	4	136—140 (decomp.)	90	37.45 (37.65)	1.75 (1.80)
(**2**)	5	122—126	76	38.90 (39.15)	2.15 (2.20)
(**3**)	6	114—116	72	40.25 (40.55)	2.70 (2.55)
(**4**)	3	118—121	49[c]	22.15 (22.50)	0.85 (0.85)
(**5**)	4	171—172	78[d]	23.75 (23.75)	1.15 (1.15)

[a] The number of methylene groups in the polymethylene chain. [b] Calculated values in parentheses. [c] By reaction of $Na[Re(CO)_5]$ with $Z(CH_2)_3Z$ ($Z = OSO_2CF_3$). [d] From $[(OC)_5ReOC(CH_2)_4CORe(CO)_5]$.

Table 2. Infrared and n.m.r. data for compounds (**1**)—(**5**)

Compound	ν(CO)[a]/cm^{-1}	^{1}H N.m.r. (δ)[b] CH_2M[c]	^{1}H N.m.r. (δ)[b] CH_2[d]	^{13}C N.m.r. (δ/p.p.m.)[b] CO	^{13}C N.m.r. (δ/p.p.m.)[b] M–CH_2	^{13}C N.m.r. (δ/p.p.m.)[b] M–CH_2CH_2	^{13}C N.m.r. (δ/p.p.m.)[b] CH_2
(**1**)	2 103w, 2 008vs, 1 980(sh)	1.06(4 H)	1.72(4 H)	213.5[e]	6.16	43.33	
(**2**)	2 105w, 2 007vs	1.08(4 H)	1.68(6 H)	213.5[e]	6.65	36.51	41.32
(**3**)	2 105w, 2 009vs, 1 979(sh)	1.12(4 H)	1.44(8 H)	213.0[e]	6.87	35.00	37.16
(**4**)	2 118w, 2 012vs, 1 974m	1.02(4 H)	2.12(2 H)	186.14, 181.55[f]	0.20	47.00	
(**5**)	2 121w, 2 011vs, 1 976m	1.01(4 H)	1.78(4 H)	186.07, 181.54[f]	9.67	49.68	

[a] Measured in $CHCl_3$. [b] Measured in $CDCl_3$. [c] Signals are broad. [d] Signals are broad multiplets. [e] Signal is weak and broad. [f] Two signals due to *cis* and *trans* carbonyls (see text).

propanediyl complexes of both manganese and rhenium starting from $ClOC(CH_2)_3COCl$ proved unsuccessful. The only products isolated in the reactions of $Na[Mn(CO)_5]$ or $Na[Re(CO)_5]$ with $ClOC(CH_2)_3COCl$ were complexes of the type $[(OC)_5M\{CO(CH_2)_3CO_2H\}]$. This result is in agreement with that obtained by Kraihanzel and Herman.[13]

Compounds (**1**)–(**5**) were all isolated as white microcrystalline solids which are stable in air for at least several months. In solvents such as thf, diethyl ether, and alcohol the compounds decompose rapidly in air to non-carbonyl species. They are however fairly stable in solution when kept under nitrogen.

The stability of compounds (**1**)—(**3**) is remarkable in comparison with some simple mononuclear manganese pentacarbonyl alkyl complexes. Ethylmanganese pentacarbonyl for example is reported to decompose slowly even when kept in the dark, *in vacuo*, and at −10 °C.[14] Green and Nagy reported that the observed decomposition product was largely propionylmanganese pentacarbonyl. Although we find that compounds (**1**)—(**3**) readily undergo CO insertion in solvents such as thf, the resulting solvated species, which may be $[(thf)(OC)_4Mn(O)C(CH_2)_nC(O)Mn(CO)_4(thf)]$, is relatively stable in solution and does not readily eliminate CO as presumably happens in the case of the ethylmanganese pentacarbonyl system.

Compounds (**1**)—(**5**) have been fully characterised by i.r., n.m.r., mass spectroscopy, and microanalysis (see Tables 1 and 2).

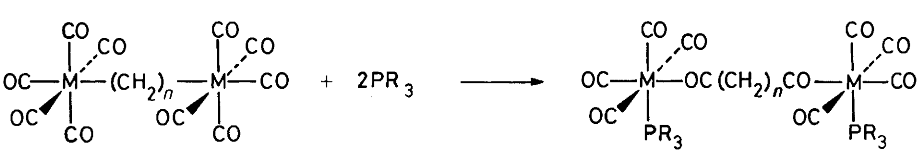
Infrared Spectra.—The i.r. spectra of the μ-alkanediyl manganese complexes show two bands for compound (**2**) and three bands for (**1**) and (**3**) in the ν(CO) region (Table 2). This is analogous to the spectra obtained for mononuclear alkylmanganese pentacarbonyl complexes.[15] The polymethylene-bridged rhenium complexes also exhibit three bands in the ν(CO) region in positions similar to those observed for methylrhenium pentacarbonyl.[16]

^{1}H *N.M.R. Spectra.*—In the ^{1}H n.m.r. spectra of compounds (**1**)—(**3**) (see Table 2) the methylene protons give rise to two signals, one a broad triplet at about δ 1.1 and a broad multiplet between δ 1.40 and 1.80. The signal at δ 1.1 corresponds to the protons of the CH_2 groups bonded to the metal centres. The broad multiplets can be assigned to the central CH_2CH_2 groups. There are small variations in the chemical shifts of the methylene protons on varying the length of the polymethylene chain. Thus as the chain length increases from complex (**1**) to (**3**), the chemical shift of Mn–CH_2 increases whereas that of the other methylene groups decreases. The chemical shifts of the methylene protons are also sensitive to changing the metal from Mn to Re (see Table 2).

^{13}C *N.M.R. Spectra.*—The proton-decoupled ^{13}C n.m.r. spectra of the complexes show two or three signals in the methylene region (see Table 2). For compound (**1**), the signal at δ 6.16 p.p.m. can be assigned to the carbon of the methylene groups which are directly bonded to the manganese atoms, by comparison with the assignments for polymethylene-bridged compounds of iron.[17] The second signal in the methylene region at δ 43.3 p.p.m. is assigned to the β-carbon atoms. The μ(1,5)-pentanediyl and μ(1,6)-hexanediyl complexes both show three signals in the methylene region of the spectrum and the assignments are given in Table 2. The spectra of the manganese μ-alkanediyl compounds also show a weak and broad signal at about δ 213 p.p.m. due to the terminal carbonyl groups if a relaxation reagent such as $[Cr(acac)_3]$ (acac = acetylacetonate) is added to the n.m.r. solution.

The ^{13}C n.m.r. spectra of the rhenium complexes (**4**) and (**5**) show only four signals. The signal at δ 186 p.p.m. can be assigned to the *cis* carbonyls while that at δ 181.5 p.p.m. is due to the *trans* carbonyls. These assignments were made on the basis of relative intensities of the peaks which in this case were approximately 4:1. This compares well with data for complexes of the type $[Re(CO)_5X]$.[18] The other signals in the spectrum are assigned in Table 2.

Mass Spectra.—Molecular ions are observed in the mass spectra of all compounds (**1**)—(**5**) but are of low intensity. The μ-alkanediyl-bis(pentacarbonyl manganese) complexes follow three fragmentation patterns: *viz.* (1) loss of CO from the parent



(5)

	n
(1)	4
(2)	5
(3)	6

	n	PR_3
(6)	4	PPh_3
(7)	4	PPh_2Me
(8)	4	$PPhMe_2$
(9)	4	PMe_3
(10)	5	PPh_3
(11)	5	PPh_2Me
(12)	5	$PPhMe_2$
(13)	6	PPh_3
(14)	6	PPh_2Me
(15)	6	$PPhMe_2$
(16)	6	PMe_3

Table 3. Yields, m.p.s, and analytical data for compounds (**6**)—(**16**)

Compound	*n*[a]	PR_3	Yield (%)	M.p. (°C)	Analysis[b] (%) C	H
(**6**)	4	PPh_3	64	118—122	61.2 (61.5)	3.90 (3.95)
(**7**)	4	PPh_2Me	80	95—96	49.90 (49.90)	4.25 (4.20)
(**8**)	4	$PPhMe_2$	66	117—120	56.45 (56.75)	4.40 (4.05)
(**9**)	4	PMe_3	83	104—108	40.45 (40.15)	4.50 (4.40)
(**10**)	5	PPh_3	68	Oil	61.80 (62.20)	4.35 (4.10)
(**11**)	5	PPh_2Me	74	Oil	56.75 (57.20)	4.40 (4.20)
(**12**)	5	$PPhMe_2$	69	Oil	50.35 (50.55)	4.20 (4.40)
(**13**)	6	PPh_3	55	112—119	62.15 (62.55)	4.35 (4.25)
(**14**)	6	PPh_2Me	68	Oil	57.30 (57.65)	4.15 (4.35)
(**15**)	6	$PPhMe_2$	61	58-61	51.20 (51.20)	4.55 (4.55)
(**16**)	6	PMe_3	58	Oil	41.95 (42.20)	4.60 (4.85)

[a] The number of methylene groups in the polymethylene chain. [b] Calculated values in parentheses.

Table 4. Infrared and ^1H n.m.r. data for the diacyl compounds (**6**)—(**16**)

Compound	ν(CO)[a]/cm^{-1}	^1H N.m.r. (δ)[b] P-Ph[c]	CH_2COM[d]	$P-CH_3$[e]	CH_2[f]
(**6**)	2 067m, 1 994s, 1 962vs, 1 604m br	7.38(30 H)	2.66(4 H)		0.88—1.24(4 H)
(**7**)	2 067m, 1 991s, 1 956 vs, 1 603m br	7.38(20 H)	2.58(4 H)	2.06(6 H)	1.10(4 H)
(**8**)	2 056 (sh), 1 985s, 1 960vs, 1 603m br	7.36(10 H)	2.73(4 H)	1.79(12 H)	1.25(4 H)
(**9**)	2 057m, 2 008s, 1 990m, 1 963s, 1 605m br		2.88(4 H)	1.46(18 H)	1.24(4 H)
(**10**)	2 068m, 1 995s, 1 962vs, 1 604m br	7.42(30 H)	2.54(4 H)		0.74—1.64(6 H)
(**11**)	2 068m, 1 991s, 1 962vs, 1 600m br	7.39(20 H)	2.66(4 H)	2.11(6 H)	0.88—1.26(6 H)
(**12**)	2 055m, 1 985 (sh), 1 957s, 1 603m br	7.38(10 H)	2.74(4 H)	1.78(12 H)	1.24(6 H)
(**13**)	2 068m, 1 996s, 1 962vs, 1 606m br	7.40(30 H)	2.75(4 H)		1.11(8 H)
(**14**)	2 067m, 1 993m, 1 963s, 1 599m br	7.38(20 H)	2.64(4 H)	2.05(6 H)	1.12(8 H)
(**15**)	2 065m, 1 988s, 1 962vs, 1 601w br	7.40(10 H)	2.78(4 H)	1.82(12 H)	1.16(8 H)
(**16**)	2 057m, 2 007s, 1 963vs, 1 603m br		2.63(4 H)	1.48(18 H)	1.20(8 H)

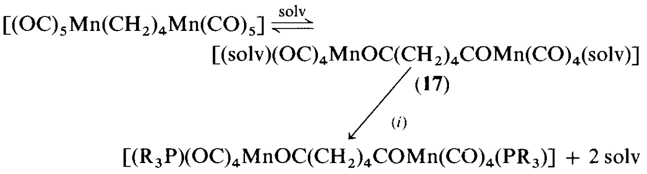
s = Strong, v = very, m = medium, sh = shoulder, br = broad, and w = weak.
[a] Measured in $CHCl_3$. [b] Measured in $CDCl_3$. [c] Signals are broad singlets. [d] Signals are broad triplets. [e] Signals are doublets (J_{H-P} = 9 Hz). [f] Signals are broad multiplets.

ion, (2) loss of the hydrocarbon bridge to form $[Mn_2(CO)_{10}]^+$, and (3) loss of a $Mn(CO)_5$ fragment from the parent ion. The fragmentation pattern of compound (**5**) resembles that of the μ(1,*n*)-alkanediyl complexes of manganese, but for compound (**4**) the major decomposition pathway involves initial elimination of C_3H_6.

Reactivity of the Complexes $[(OC)_5M(CH_2)_nM(CO)_5]$ (M = Mn, *n* = 4—6; M = Re, *n* = 4).—(*a*) $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ *with tertiary phosphines*, PR_3. As for mononuclear manganese pentacarbonyl alkyls,[19] the reactions of $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ (*n* = 4—6) with tertiary phosphines yield bis(phosphine) diacyl compounds [equation (5)]. The reactions proceed rapidly and almost quantitatively at room temperature. The phosphine-substituted complexes were isolated as either white microcrystalline solids or clear oils and characterized by i.r., ^1H n.m.r. spectroscopy and microanalysis (see Tables 3 and 4). They are stable at room temperature in pure form but decompose rapidly in solution in the presence of air.

The i.r. spectra are similar to those of mononuclear compounds $[Mn(CO)_4(COR)(PR_3)]$,[20] showing four bands in the ν(CO) region which is indicative of a *cis* configuration of ligands around *both* manganese atoms. The observation of only *cis* isomers indicates that the *cis–trans* isomerisation for the binuclear compounds is not so facile as for mononuclear monoacyls.[21]

It has been shown for methyl manganese pentacarbonyl that the rate of 'CO insertion' is enhanced when the reaction is carried out in polar, co-ordinating solvents.[22] We find similar results for complexes (**1**)—(**3**) with PR_3 ligands in thf. As is the case for mononuclear alkylmanganese pentacarbonyl complexes, we suspect that the reactions of the μ-polymethylene compounds proceed *via* the reaction pathway outlined in Scheme 1. Evidence for the solvent-stabilized intermediate, (**17**), is obtained from i.r. studies. Thus, when $[(OC)_5Mn(CH_2)_4Mn(CO)_5]$ is dissolved in thf, ν(CO) of an acyl species is clearly seen; however the compound decomposed on attempted isolation.



Scheme 1. solv = thf; (*i*) PR_3

A comparison of the reaction times of tertiary phosphines with $[\{Mn(CO_5)\}_2\{\mu\text{-}(CH_2)_n\}]$ and $[MnMe(CO)_5]$ shows that the former are much shorter. This suggests that the $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_n\}]$ complexes are more reactive than $[MnMe(CO)_5]$ towards PR_3 ligands.

The ^1H n.m.r. spectra for PR_3-substituted diacyl compounds (**6**)—(**16**) are similar to those for $[Mn(CO)_4(COR')(PR_3)]$ complexes.[20]

Compounds (**6**)—(**9**) were decarbonylated thermally to form tertiary phosphine-substituted μ(1,4)-butanediyl species. The reaction proceeds smoothly and quantitatively in about 15 min in refluxing hexane [equation (6)]. The compounds were isolated as white microcrystalline solids and are stable in the solid state, only decomposing in solution after prolonged exposure to air. Their i.r. spectra show four bands in the ν(CO) region, suggesting that they also exist as *cis-cis* isomers.

$$[(R_3P)(OC)_4MnOC(CH_2)_4COMn(CO)_4(PR_3)] \longrightarrow [(R_3P)(OC)_4Mn(CH_2)_4Mn(CO)_4(PR_3)] + 2CO \tag{6}$$

	PR_3
(**18**)	PPh_3
(**19**)	PPh_2Me
(**20**)	$PPhMe_2$
(**21**)	PMe_3

(*b*) $[(OC)_5Re(CH_2)_4Re(CO)_5]$ *with tertiary phosphones.* The reactions of $[\{Re(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (**5**) with tertiary phosphines proceed much slower than those of the analogous manganese μ(1,4)-butanediyl complex, *e.g.* the reaction with PPh_3 yields (**22**) after refluxing for 42 h in thf [equation (7)]. In the case of the $PPhMe_2$ reaction, it is possible to isolate the intermediate disubstituted diacyl complex $[(L)(OC)_4ReOC(CH_2)_4CORe(CO)_4(L)]$ (L = $PPhMe_2$).

$$[\{Re(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}] + 2PR_3 \longrightarrow [\{Re(CO)_4(PR_3)\}_2\{\mu\text{-}(CH_2)_4\}] + 2CO \tag{7}$$

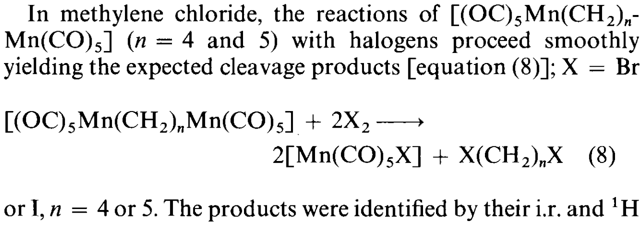
	PR_3
(**22**)	PPh_3
(**23**)	PPh_2Me
(**24**)	$PPhMe_2$

The slowness of the reactions of the rhenium μ(1,4)-butanediyl complex in comparison with those of manganese is in agreement with the general observation that alkyl complexes of third-row elements undergo alkyl migration and substitution reactions at rates much slower than those of first-row elements.[23]

Compounds (**22**)—(**24**) were isolated as white microcrystalline solids, which were characterised by microanalysis, i.r. and ^1H n.m.r. spectroscopy (Tables 5 and 6).

(*c*) *With halogens.* There are very few reports in the literature on the reactions of mononuclear alkyl complexes of manganese and rhenium with halogens. On the other hand the reactions of both mononuclear and μ(1,*n*)-alkanediyl di-iron complexes have been investigated extensively.[24,25] These iron complexes react with halogen (X_2) to give $[Fe(cp)(CO)_2X]$ (cp = η^5-C_5H_5) and the appropriate dihalogenoalkane.

We find that when complex (**1**) was treated with Br_2 or I_2 in a 1:2 mole ratio in thf as solvent the expected cleavage products were *not* obtained and, instead, adipic acid and an unidentified inorganic product were isolated. The adipic acid can be accounted for by the reaction sequence in Scheme 2.



Scheme 2. (*i*) thf; (*ii*) hydrolysis on work up

In methylene chloride, the reactions of $[(OC)_5Mn(CH_2)_nMn(CO)_5]$ (n = 4 and 5) with halogens proceed smoothly yielding the expected cleavage products [equation (8)]; X = Br or I, n = 4 or 5. The products were identified by their i.r. and ^1H n.m.r. spectra and by comparison with authentic samples. The rhenium complex $[(OC)_5Re(CH_2)_4Re(CO)_5]$ (**5**) also reacts with halogens to give the expected cleavage product in thf.

$$[(OC)_5Mn(CH_2)_nMn(CO)_5] + 2X_2 \longrightarrow 2[Mn(CO)_5X] + X(CH_2)_nX \tag{8}$$

(*d*) *With carbon monoxide.* The reactions of mononuclear manganese alkyl complexes with carbon monoxide are well known.[25] These complexes undergo alkyl migration reactions to form the acyl derivatives. The mechanism of this reaction has been investigated extensively[26] and it is believed that it involves an alkyl migration rather than a CO insertion.[4] The reaction of complex (**1**) with CO (1 atm) readily yields the diacyl compound in thf [equation (9)]. This reaction is reversible since on heating the μ-alkanediyl complex can be isolated. We are at present measuring the rates of the forward and back reactions.[27]

$$[(OC)_5Mn(CH_2)_4Mn(CO)_5] \underset{heat}{\overset{CO}{\rightleftharpoons}} [(OC)_5MnOC(CH_2)_4COMn(CO)_5] \tag{9}$$

The μ(1,4)-butanediyl complex of rhenium, (**5**), reacts very sluggishly with carbon monoxide. Thus at 40 atm CO for 24 h only about 30% of the diacyl species $[(OC)_5ReOC(CH_2)_4CORe(CO)_5]$ is obtained.

(*e*) $[\{Mn(CO)_5\}\{\mu\text{-}(CH_2)_4\}]$ *with synthesis gas.* The complex $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (**1**) was treated with synthesis gas (1:1 mixture of CO and H_2) at 40 atm and 70 °C, using thf as

Table 5. Yields, m.p.s, and analytical data for compounds (**18**)—(**24**)

Compound	M	PR_3	Yield (%)	M.p. (°C)	Analysis* (%) C	Analysis* (%) H
(**18**)	Mn	PPh_3	81	137—140	62.75 (63.05)	4.30 (4.15)
(**19**)	Mn	PPh_2Me	88	116—121	57.35 (57.70)	3.95 (4.30)
(**20**)	Mn	$PPhMe_2$	64	128—131	50.15 (50.45)	4.30 (4.50)
(**21**)	Mn	PMe_3	77	123—126	39.55 (39.85)	4.70 (4.80)
(**22**)	Re	PPh_3	68	154—159	49.30 (49.00)	3.55 (3.25)
(**23**)	Re	PPh_2Me	60	148—154	43.30 (43.35)	3.15 (3.25)
(**24**)	Re	$PPhMe_2$	56	92—98	36.45 (36.20)	3.50 (3.30)

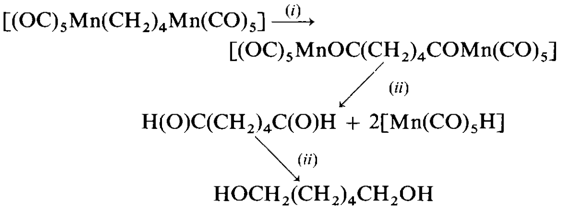
* Calculated values in parentheses.

Table 6. Infrared and ^1H n.m.r. data for compounds (**18**)—(**24**)

Compound	$\nu(CO)^a/cm^{-1}$	^1H N.m.r. $(\delta)^b$ P–Ph^c	CH_2M^d	$CH_2{}^d$	$P-CH_3{}^e$
(**18**)	2 051w, 1 978m, 1 964s, 1 935m	7.10(30 H)	0.30(4 H)	1.24(4 H)	
(**19**)	2 052m, 1 980m, 1 963s, 1 936m	7.34(20 H)	0.45(4 H)	1.38(4 H)	1.86(6 H)
(**20**)	2 052w, 1 978m, 1 961s, 1 941 (sh), 1 931m	7.36(10 H)	0.54(4 H)	1.50(4 H)	1.74(12 H)
(**21**)	2 052w, 1 977m, 1 961s, 1 934m		0.80(4 H)	1.88(4 H)	1.26(18 H)
(**22**)^f	2 073m, 1 980s (sh), 1 969vs, 1 922s	7.28(30 H)	0.40—0.43(4 H)	1.39(4 H)	
(**23**)^f	2 072m, 1 978s (sh), 1 968vs, 1 922m	7.33(20 H)	0.5(4 H)	1.49(4 H)	2.02(6 H)
(**24**)^f	2 071m, 1 978s (sh), 1 969vs, 1 920m	7.40(10 H)	0.86(4 H)	1.60(4 H)	1.84(12 H)

[a] Measured in hexane unless stated otherwise. [b] Measured in $CDCl_3$. [c] Signals are broad singlets. [d] Signals are broad multiplets. [e] Signals are doublets ($^2J_{PH}$ = 9 Hz). [f] Measured in CH_2Cl_2.

solvent. The reaction yields the diol $HOCH_2(CH_2)_4CH_2OH$ as the only isolable organic product. A small amount of an aldehyde species [ν(CO) 1 720 cm^{-1}] was also detected by i.r. spectroscopy, however it was not possible to isolate this compound. The formation of 1,6-hexanediol can be explained by Scheme 3. The step in which the acyl intermediate $[(OC)_5MnOC(CH_2)_4COMn(CO)_5]$ is reduced to the dialdehyde has been confirmed by treating the diacyl species with hydrogen in a separate experiment. The product of this reaction is again $HOCH_2(CH_2)_4CH_2OH$. The only organometallic compound isolated is $[Mn_2(CO)_{10}]$ which may be derived from the decomposition of $[Mn(CO)_5H]$ under the conditions of the experiment. These reactions show that bifunctional organic compounds can be obtained from reactions of these alkanediyl complexes. Also, in the reaction of $[\{Mn(CO)_5\}_2\{\mu-(CH_2)_4\}]$ with synthesis gas the initial CO insertion is followed by Mn–C(O) bond cleavage by H_2. There is no evidence for reduction of the acyl CO to CH_2 under these conditions. Thus, if the alkanediyl complex is a model for a $(CH_2)_4$ fragment on a catalyst surface then the CO insertion step would result in termination rather than propagation of the hydrocarbon chain.



$$[(OC)_5Mn(CH_2)_4Mn(CO)_5] \xrightarrow{(i)} [(OC)_5MnOC(CH_2)_4COMn(CO)_5] \xrightarrow{(ii)} H(O)C(CH_2)_4C(O)H + 2[Mn(CO)_5H] \xrightarrow{(ii)} HOCH_2(CH_2)_4CH_2OH$$

Scheme 3. (*i*) CO; (*ii*) H_2

Experimental

All reactions were carried out under an atmosphere of nitrogen using Schlenk-tube techniques. The compounds $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$ purchased from Strem Chemicals, U.S.A., and the diacyl chlorides from Aldrich Chemicals, were used without further purification; $Z(CH_2)_3Z$ ($Z = OSO_2CF_3$) was prepared using a literature method.[28] Tetrahydrofuran was distilled over sodium wire under nitrogen.

I.r. spectra were recorded on a Perkin-Elmer 983 spectrophotometer, n.m.r. spectra on a Bruker W90 or a Varian XL200 spectrometer. 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 and are uncorrected. Microanalyses were performed in the microanalytical laboratory at the University of Cape Town.

Synthesis of $[(OC)_5MnOC(CH_2)_nCOMn(CO)_5]$ (n = 4—6): *General Procedure*.—The above compounds were prepared using modified literature procedures[12,13] as outlined below.

The compound $[Mn_2(CO)_{10}]$ (1.5 g, 3.85 mmol) in thf (25 cm^3) was stirred over sodium amalgam (0.3 g Na in 6 cm^3 Hg) for 2 h at room temperature. The resulting solution of $Na[Mn(CO)_5]$ (7.70 mmol) was transferred by syringe to a Schlenk tube and the diacyl chloride $ClCO(CH_2)_nCOCl$ (n = 4—6) (3.85 mmol) was added with rapid stirring. The reaction mixture was stirred for 3 h at room temperature. The solvent was removed leaving a yellow residue which was extracted with warm chloroform (50 cm^3) and filtered. The filtrate was concentrated to *ca.* 10 cm^3 and hexane added until the solution became cloudy. Cooling (−15 °C) resulted in the formation of the diacyl complexes $[(OC)_5MnOC(CH_2)_nCOMn(CO)_5]$ (n = 4—6).

Synthesis of the μ-*Alkanediyl Complexes* $[\{Mn(CO)_5\}_2\{\mu-(CH_2)_n\}]$ (n = 4—6) (**1**—**3**).—The diacyl compounds $[(OC)_5MnOC(CH_2)_nCOMn(CO)_5]$ (n = 4—6) were converted into the corresponding $\mu(1,n)$-alkanediyl compounds by decarbonylation. This is effected by refluxing the diacyl complex in hexane for about 15 min. In a typical preparation, $[(OC)_5MnOC(CH_2)_nCOMn(CO)_5]$ (2 mmol) was suspended in hexane (150 cm^3) then refluxed for 15 min under nitrogen. The reaction can be followed by i.r. spectroscopy, by monitoring the disappearance of the acyl band around 1 625 cm^{-1}. Removal of the hexane leaves a cream solid which can be recrystallised by dissolving in a minimum of chloroform and adding hexane. Cooling to −15 °C results in the formation of a white microcrystalline solid. The yields, melting points, elemental analysis, and spectroscopic data are given in Tables 1 and 2.

Synthesis of $[(OC)_5ReOC(CH_2)_4CORe(CO)_5]$.—The compound $[Re_2(CO)_{10}]$ (1 g, 1.53 mmol) in thf (30 cm^3) was stirred over sodium amalgam (0.2 g Na in 4 cm^3 Hg) for 2 h at room temperature. The resulting orange solution of $Na[Re(CO)_5]$ (3.06 mmol) was transferred by syringe to a Schlenk tube. Adipoyl dichloride (0.28 g, 1.53 mmol) was added dropwise with rapid stirring. The solution becomes cloudy almost immediately with a precipitate. It was stirred for 3 h at room temperature then the solvent was removed leaving a creamy white residue. This was extracted with methylene chloride and filtered. The filtrate was taken to dryness leaving a white solid, which was recrystallised from warm acetone. The resulting white microcrystalline solid was filtered off to give 0.7 g (60%) of $[(OC)_5ReOC(CH_2)_4CORe(CO)_5]$, m.p. 143—147 °C (Found: C, 24.8; H, 1.1. Calc. for $C_{16}H_8O_{12}Re_2$: C, 25.1; H, 1.1%): ν(CO) ($CHCl_3$) 2 133w, 2 023vs, and 1 605w br cm^{-1}. ^1H n.m.r. ($CDCl_3$); δ 2.68 (t, 4 H, CH_2CO) and 1.38 (m, 4 H, CH_2).

Conversion of $[(OC)_5ReOC(CH_2)_4CORe(CO)_5]$ *into* $[\{Re(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$.—The complex $[(OC)_5ReOC(CH_2)_4CORe(CO)_5]$ (0.7 g, 0.92 mmol) was suspended in toluene (100 cm^3) and refluxed for 1 h. The reaction mixture was filtered while hot and the filtrate reduced to *ca.* 30 cm^3. It was then cooled to *ca.* 15 °C which resulted in the formation of white crystals. These were filtered off to give the μ-alkanediyl complex. The yield and characterisation data are recorded in Tables 1 and 2.

Synthesis of $[\{Re(CO)_5\}_2\{\mu\text{-}(CH_2)_3\}]$ (**4**).—The compound $[Re_2(CO)_{10}]$ (0.5 g, 0.77 mmol) in thf (20 cm^3) was stirred over sodium amalgam (0.1 g Na in 2 cm^3 Hg) for 2 h under nitrogen at room temperature. The resulting solution of $Na[Re(CO)_5]$ (1.54 mmol) was transferred to another Schlenk tube. A solution of $F_3CO_2SO(CH_2)_3OSO_2CF_3$ (0.26 g, 0.77 mmol) in thf (5 cm^3) was added dropwise with rapid stirring. The reaction mixture was stirred for 3 h at room temperature. The solvent was removed, leaving a light yellow residue which was extracted with chloroform (40 cm^3) and filtered. The filtrate was taken to dryness leaving a white residue which was recrystallised from chloroform–hexane to give complex (**4**) in 49% yield. Characterisation data are listed in Tables 1 and 2.

Reactions of $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_n\}]$ (n = 4—6), (**1**)—(**3**), *with Tertiary Phosphines,* PR_3 (1:2 *mole ratio*): *General Procedure.*—The complex $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_n\}]$ (0.45 mmol) was dissolved in thf (10 cm^3). A solution of the tertiary phosphine (0.90 mmol) in thf (2 cm^3) was added and the mixture stirred at room temperature for between 45 and 90 min. The reaction was monitored by i.r. spectroscopy and continued until no more starting material remained. The solvent was removed leaving a colourless oily residue which was extracted with chloroform and filtered. The filtrate was taken to dryness, leaving a sticky residue. In the case of the reactions of the compounds where $n = 4$ and $n = 6$ ($PR_3 = PPhMe_2$ or PMe_3), the products could be purified by adding hexane to the oil. This results in a white microcrystalline solid. In the cases where $n = 5$ or $PR_3 = PPh_2Me$ the products are oils at room temperature and were purified by adding hexane to the oily residue and then cooling to −78 °C. This resulted in a white solid precipitate. The supernatant was removed by syringe and the white solid washed with ice-cold hexane (3 × 5 cm^3). The washings were then syringed off. The solid was allowed to warm to room temperature. On doing so the solid melts to yield a colourless oil. The product was dried under vacuum. The yields, melting points, microanalysis, and spectral data for compounds (**6**)—(**16**) are given in Tables 3 and 4.

Preparation of $[\{Mn(CO)_4(PR_3)\}_2\{\mu\text{-}(CH_2)_4\}]$ (**18**)—(**21**).—The phosphine-substituted diacyl compounds (**6**)—(**9**), were converted into the corresponding phosphine-substituted μ-alkanediyl compounds (**18**)—(**21**) according to the following general procedure.

The compound $[(R_3P)(OC)_4MnOC(CH_2)_4COMn(CO)_4(PR_3)]$ (0.1 g) was suspended in hexane (20 cm^3) then refluxed for *ca.* 1 h. The reaction was monitored by i.r. spectroscopy in the region 2 200—1 550 cm^{-1}. Heating was continued until the acyl band at 1 605 cm^{-1} had completely disappeared. The reaction mixture was allowed to cool to room temperature and the solvent removed under reduced pressure. The oily pale yellow residue was dissolved in a minimum of CH_2Cl_2 and filtered. Addition of hexane and cooling (−15 °C) resulted in a white microcrystalline solid identified as $[\{Mn(CO)_4(PR_3)\}_2\{\mu\text{-}(CH_2)_4\}]$ (**18**)—(**21**). The melting points and elemental analysis of the products are given in Table 5 and the i.r. and ^1H n.m.r. data in Table 6.

Reactions of $[\{Re(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (**5**) *with Tertiary Phosphines* (1:2 *mole ratio*): *General Method.*—A solution of the tertiary phosphine (1 mmol) in thf (2 cm^3) was added to a solution of $[\{Re(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (0.5 mmol) in thf (10 cm^3). The mixture was refluxed under nitrogen. The course of the reaction was followed by i.r. spectroscopy in the region 2 200—1 500 cm^{-1}. The reaction was continued until the i.r. spectrum showed no further change; this takes between 2.5 and 6 d depending on the tertiary phosphine used. The reaction mixture was allowed to cool and the solvent removed. This leaves an oily residue which was extracted with methylene chloride and filtered. The filtrate was taken to dryness to yield a sticky residue which was triturated with hexane (5 cm^3), resulting in a white solid. This solid was filtered off and dried. Analytically pure samples were obtained by recrystallisation from CH_2Cl_2–hexane at −78 °C. The yields, elemental analysis, and spectral data are in Tables 5 and 6.

Reactions of $[\{M(CO)_5\}_2\{\mu\text{-}(CH_2)_n\}]$ (M = Mn, n = 4—6; M = Re, n = 4) *with Halogens,* X_2 (X = Br *or* I).—(*a*) $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (**1**) *with* Br_2 *and* I_2 *in thf.* Compound (**1**) (0.1 g, 0.22 mmol) was dissolved in thf (10 cm^3). A solution of Br_2 (0.44 mmol) in thf (2 cm^3) was added with rapid stirring. The mixture was stirred for 1 h at room temperature. The solvent was removed leaving a brown residue. Methylene chloride (15 cm^3) was added to the residue resulting in a fine off-white precipitate. This solid was filtered off, washed with a minimum of dichloromethane, and dried on the water pump to yield 0.022 g (69%) of adipic acid, which was identified by comparing its i.r. and ^1H n.m.r. spectra with those of authentic samples. The filtrate obtained above was taken to dryness leaving a brown residue, an i.r. spectrum of which revealed that it is a non-carbonyl-containing species, which we were unable to identify.

A similar result to the one above was obtained when complex (**1**) was treated with I_2 in thf; the organic product isolated was again adipic acid (56%).

The reaction of complex (**2**) with Br_2 was also performed in thf. This yields pimelic acid, $HO_2C(CH_2)_5CO_2H$ (60%), identified on the basis of its i.r. and ^1H n.m.r. spectra.

(*b*) $[\{M(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (M = Mn *or* Re) *with halogens in methylene chloride, general procedure.* The compound $[\{M(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (0.22 mmol) was dissolved in anhydrous methylene chloride (10 cm^3). A solution of the halogen X_2 (0.44 mmol) in methylene chloride (2 cm^3) was added with rapid stirring at room temperature. The orange-red solution was stirred for 1 h at this temperature. The volume of the reaction mixture was reduced to *ca.* 3 cm^3, then chromatographed on a silica gel column (made up in hexane). Elution with CH_2Cl_2–hexane (1:1) gave two bands, *viz.* a pale yellow band and a yellow-orange band. The eluted solutions were evaporated to dryness and the products identified by comparison with authentic samples as described below.

Reaction of $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (**1**) *with* X_2.—A solution of Br_2 (0.44 mmol) in CH_2Cl_2 (2 cm^3) was added to a solution of complex (**1**) in CH_2Cl_2 (10 cm^3) at room temperature. The reaction was worked up using the procedure outlined above. A pale yellow band eluted with CH_2Cl_2–hexane (1:1) gave a pale yellow oil on removal of the solvent. This was identified as $Br(CH_2)_4Br$ on the basis of its i.r. and ^1H n.m.r. spectra. A yellow-orange band was eluted with 20% hexane in CH_2Cl_2. This yielded a yellow solid on evaporation of the solution, the i.r. spectrum of which was identical to that of $[Mn(CO)_5Br]$ (74% yield).

The reaction of complex (**1**) with I_2 in CH_2Cl_2 was carried out in an analogous fashion. The products isolated were $I(CH_2)_4I$ and $[Mn(CO)_5I]$ (82% yield).

Reaction of $[\{Re(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (**5**) *with* X_2.—A solution of Br_2 (0.4 mmol) in CH_2Cl_2 (2 cm^3) was added to a solution of complex (**5**) (0.2 mmol) in CH_2Cl_2 (10 cm^3) at room temperature (20 °C). The reaction mixture was worked up as described earlier. Again two bands were separated on the column. The first (pale yellow) band yields a yellow oil on evaporation of the solution. This was identified as $Br(CH_2)_4Br$ on the basis of its i.r. and proton n.m.r. spectra. A second faint yellow band was eluted with pure CH_2Cl_2. This yields a pale yellow solid, identified as $[Re(CO)_5Br]$ (72% yield).

Similarly the reaction of complex (**5**) with I_2 in CH_2Cl_2 yields $I(CH_2)_4I$ and $[Re(CO)_5I]$ (68% yield).

Reaction of $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (**1**) *with Carbon Monoxide.*—Compound (**1**) (0.15 g, 0.34 mmol) was dissolved in thf (20 cm^3), then CO was bubbled through the mixture for 30 min. The reaction mixture was then stirred for an additional 1.5 h at room temperature. The solvent was removed to yield a white solid which was recrystallised from $CHCl_3$–hexane to yield 90% of the diacyl species $[(OC)_5MnOC(CH_2)_4COMn(CO)_5]$.

Reaction of $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ *with Synthesis Gas.*—This reaction was carried out in a Berghof autoclave (250 cm^3) charged with $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ (0.1 g, 0.22 mmol) and thf (15 cm^3). The autoclave was pressurised with synthesis gas (CO–H_2, 1:1) (40 atm.), then heated to 70 °C for 3.5 h. It was allowed to cool to room temperature and the gases vented. A dark brown mixture was obtained which was filtered yielding a pale yellow filtrate. Solvent was removed from the filtrate, leaving a pale yellow oil. An i.r. spectrum (neat film) of the oily residue shows that it is a mixture of $HOCH_2(CH_2)_4CH_2OH$ and $[Mn_2(CO)_{10}]$, with the diol being the major component. The oil was dissolved in a minimum of CH_2Cl_2–hexane (1:1). The solution was then filtered through a short (5 cm) alumina column (made up with hexane). Two bands were observed on the column, a faint yellow (almost colourless) band and a bright yellow band. The former was eluted with 10% CH_2Cl_2–hexane and on evaporation gave a pale yellow oil, identified as $HOCH_2(CH_2)_4CH_2OH$ on the basis of its i.r. and ^1H n.m.r. spectra (yield 69%). The second yellow band was eluted with CH_2Cl_2 and evaporation of the solution produced a trace of a yellow solid, the i.r. spectrum of which was identical to that of $[Mn_2(CO)_{10}]$.

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