

Mononuclear alkyl and acyl derivatives of rheniopentacarbonyl: synthesis, characterization and properties

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Abstract

The extensive homologous series of acyl and *n*-alkyl compounds, $[\text{Re}(\text{COR})(\text{CO})_5]$ and $[\text{Re}(\text{R})(\text{CO})_5]$ ($\text{R} = \text{CH}_3$ to $n\text{-C}_{18}\text{H}_{37}$), has been synthesized. The majority of the compounds are new and have been fully characterized by elemental analysis, IR, ^1H and ^{13}C NMR and mass spectrometry. The data for the series are discussed. Some properties of the compounds are described, including reactions of the alkyl compounds with PPh_3 , which yield *cis*- $[\text{Re}(\text{R})(\text{CO})_4(\text{PPh}_3)]$ and *not cis*- $[\text{Re}(\text{COR})(\text{CO})_4(\text{PPh}_3)]$ as might have been expected.

Keywords: Rhenium; Carbonyl; Alkyl; Acyl

1. Introduction

Transition metal alkyl and acyl compounds have been studied extensively because of (a) their fundamental importance in chemistry and (b) their significance as models for metal alkyl and acyl intermediates in a wide variety of industrially important catalytic reactions. These reactions include the Fischer-Tropsch synthesis, the hydrogenation and hydroformylation of olefins, and the Monsanto acetic acid synthesis.

However, while numerous studies on metal alkyl compounds, L_nMR , have been reported the vast majority of these have been on short chain alkyl (SCA) compounds ($\text{R} = \text{CH}_3$, C_2H_5 or C_3H_7). Very few studies have been reported on long chain alkyl (LCA) compounds ($\text{R} \geq \text{C}_4\text{H}_9$) [1–3]. Whereas studies on the SCA compounds can provide us with information about chain growth processes in catalytic reactions, studies on LCA compounds may have more significance for chain termination steps. In view of the importance of chain termination steps in catalytic reactions, such as in polymerization reactions where a specific polymer chain length may be required, it is surprising that there have been so few studies of LCA transition metal compounds. This is even more remarkable when one consid-

ers the fact that some reactions of metal alkyl compounds that are key reactions in catalysis are dependent on the alkyl chain length. Examples include the rate of CO insertion in $[\text{Mn}(\text{R})(\text{CO})_5]$ [3,4] and C_2H_4 insertion into $\text{Sc}-\text{C}$ in $[\text{Cp}_2^+\text{ScR}]$ [5]. Also, theoretical studies by Berke and Hoffmann show that activation parameters for alkyl migration in transition metal alkyl compounds are a function of the chain length of the alkyl group [6].

We now report the synthesis and characterization of an extensive homologous series of mononuclear rhenium pentacarbonyl acyl and alkyl compounds, $[\text{Re}(\text{COR})(\text{CO})_5]$ and $[\text{Re}(\text{R})(\text{CO})_5]$ (where $\text{R} = \text{CH}_3$ to $n\text{-C}_{18}\text{H}_{37}$). Until now, the only known mononuclear rhenium pentacarbonyl species of the type $[\text{Re}(\text{R})(\text{CO})_5]$ (where R is a hydrocarbyl ligand) have been $[\text{Re}(\text{CH}_3)(\text{CO})_5]$, $[\text{Re}(\text{C}_6\text{H}_5)(\text{CO})_5]$, $[\text{Re}(\text{CH}_2\text{C}_6\text{H}_5)(\text{CO})_5]$ [7], $[\text{Re}(\text{C}_2\text{H}_5)(\text{CO})_5]$ [8], $[\text{Re}(\text{C}_2\text{H}_4)(\text{CO})_5]^+$ [9,10], $[\text{Re}(i\text{-C}_4\text{H}_9)(\text{CO})_5]$ [11] and some substituted benzyl and phenyl derivatives [12–15]. The acyl complexes $[\text{Re}(\text{COCH}_3)(\text{CO})_5]$, $[\text{Re}(\text{COC}_6\text{H}_5)(\text{CO})_5]$, $[\text{Re}(\text{COCH}_2\text{C}_6\text{H}_5)(\text{CO})_5]$ [7] and $[\text{Re}(\text{COC}_2\text{H}_5)(\text{CO})_5]$ [8] have also been described.

Although numerous reactions have been reported for $[\text{Mn}(\text{R})(\text{CO})_5]$ compounds [16], particularly $[\text{Mn}(\text{CH}_3)(\text{CO})_5]$, very few are known for the corresponding $[\text{Re}(\text{R})(\text{CO})_5]$ species. It has been observed that alkyl complexes of third row transition metals undergo alkyl migration or substitution reactions at rates much slower

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than those for first row metals [17,18]. This is partly because of the higher strength of the metal–carbon alkyl bond in $[\text{Re}(\text{R})(\text{CO})_5]$ than in $[\text{Mn}(\text{R})(\text{CO})_5]$ [19], which has been correlated with an increase in the bonding overlaps between the 2σ R and the (p, d)-hybrid σML_n on the metal centre [20].

In view of the fact that we were able to synthesize higher *n*-alkyl derivatives of $[\text{Mn}(\text{CO})_5]$ and found them to be relatively stable [2,3], we were interested in investigating the rhenium analogues in order to determine the effects of (a) changing the metal atom in $[\text{M}(\text{R})(\text{CO})_5]$ and $[\text{M}(\text{COR})(\text{CO})_5]$ and (b) variation of the length of the alkyl chain in $[\text{Re}(\text{R})(\text{CO})_5]$ on the rate of reaction with a nucleophile. We hoped that this would generate new information relevant to the alkyl migration reaction and on the nature of transition metal alkyl compounds in general.

2. Experimental details

2.1. General procedures

All reactions were carried out under nitrogen using standard Schlenk tube techniques. Tetrahydrofuran (THF) was distilled from sodium before use, toluene was distilled from calcium chloride. The alkyl halides and acyl halides were obtained from Aldrich and were used without purification. Triphenylphosphine was obtained from Merck, and $[\text{Re}_2(\text{CO})_{10}]$ from Strem.

Alumina (BDH, active neutral, Brockman grade 1) was deactivated before use. Melting points were recorded on a Kofler hot-stage microscope (Reichert Thermovar) and are uncorrected. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer and ^1H and ^{13}C NMR spectra on a Varian XR 200 spectrometer. Mass spectra were obtained with a VG Micromass 16F spectrometer, operating at 70 eV ionizing voltage. The source temperature was raised from room temperature until the spectrum was observed. Tables of mass spectra are available from the authors.

2.2. General method for the preparation of $[\text{Re}(\text{COR})(\text{CO})_5]$ ($\text{R} = \text{CH}_3$ to $n\text{-C}_9\text{H}_{19}$; $n\text{-C}_{11}\text{H}_{23}$; $n\text{-C}_{13}\text{H}_{27}$; $n\text{-C}_{15}\text{H}_{31}$; $n\text{-C}_{17}\text{H}_{35}$)

A solution of $\text{Na}[\text{Re}(\text{CO})_5]$ (3.06 mmol) in THF (25 ml) was added dropwise with stirring during 5 min to the acyl chloride, RCOCl (ca. 3.05 mmol) at 0°C . The solution went cloudy almost immediately as a precipitate formed. The solution was stirred for a further 3 h at room temperature and the solvent then removed under reduced pressure to leave a pale yellow residue. This was extracted with CH_2Cl_2 (2×30 ml) and the extract

centrifuged for ca. 10 mins. The solvent was removed from the extract under reduced pressure to give a pale yellow solid, which was extracted with hexane (ca. 15 ml). The extract was filtered, and kept at -78°C to deposit crystals. The products in all cases were pale-yellow solids.

2.3. General method for the preparation of $[\text{Re}(\text{R})(\text{CO})_5]$ ($\text{R} = \text{CH}_3$ to $n\text{-C}_9\text{H}_{19}$; $n\text{-C}_{11}\text{H}_{23}$; $n\text{-C}_{13}\text{H}_{27}$; $n\text{-C}_{15}\text{H}_{31}$; $n\text{-C}_{17}\text{H}_{35}$)

A solution of $[\text{Re}(\text{COR})(\text{CO})_5]$ (1.0 g) in toluene (50 ml) was refluxed for 4 h under N_2 , then cooled to room temperature. The solvent was removed under reduced pressure to give the product either as a yellow oil, or as a yellow solid that was recrystallized from hexane at -78°C .

2.4. General method for the preparation of $[\text{Re}(\text{R})(\text{CO})_5]$ ($\text{R} = n\text{-C}_{10}\text{H}_{21}$; $n\text{-C}_{12}\text{H}_{25}$; $n\text{-C}_{18}\text{H}_{37}$; $n\text{-C}_{16}\text{H}_{33}$; $n\text{-C}_{18}\text{H}_{37}$)

A solution of $\text{Na}[\text{Re}(\text{CO})_5]$ (3.38 mmol) in THF (20 ml) was added dropwise with stirring during 5 min to the alkyl bromide, RBr (ca. 3.37 mmol) at 0°C . The solution rapidly went cloudy as a precipitate formed. The solution was stirred for a further 8 h at room temperature and the solvent then removed under reduced pressure to leave a pale-yellow residue. This was extracted with CH_2Cl_2 (2×30 ml) and the extract was centrifuged for ca. 10 min. The solvent was removed from the extract under reduced pressure to give a pale-yellow solid, which was extracted with hexane (ca. 20 ml). The extract was filtered and kept at -78°C to deposit crystals. The product in each case was a cream or yellow solid.

2.5. General method for the reaction of $[\text{Re}(\text{R})(\text{CO})_5]$ with PPh_3 ($\text{R} = \text{C}_2\text{H}_5$ to $n\text{-C}_{18}\text{H}_{37}$)

Attempts were made to monitor the reaction of the $[\text{Re}(\text{R})(\text{CO})_5]$ with PPh_3 by IR spectroscopy in order to measure the rate constants for the reactions. Typically, 5 ml of a 0.04 M toluene solution of $[\text{Re}(\text{R})(\text{CO})_5]$ was placed in a constant temperature bath at 94°C and a nine-fold molar excess of PPh_3 was added. The disappearance of the highest energy (A_1) carbonyl band was followed. It was established that the reactions all went to completion and the phosphine-substituted alkyl products, *cis*- $[\text{Re}(\text{R})(\text{CO})_4(\text{PPh}_3)]$, were formed. These were all relatively high-melting yellow solids.

2.6. Preparation of *cis*- $[\text{Re}\{\text{CO}(n\text{-C}_6\text{H}_{13})\}(\text{CO})_4(\text{PPh}_3)]$

The phosphine-substituted dimer $[\text{Re}(\text{CO})_4(\text{PPh}_3)]_2$ was prepared by a previously published procedure [21].

Table 1
Data for $[\text{Re}(\text{COR})(\text{CO})_5]$

R	Compound no.	Yield (%)	M.P. (°C)	IR $\nu(\text{CO})$ (cm^{-1}) ^a	Elemental analysis	
					C; found (calc.)	H; found (calc.)
CH_3	1	45	79–82	2131w, 2060w, 2016s, 1999ms, 1621w	22.1(22.8)	0.8(0.8)
C_2H_5	2	58	90 ^b	2130w, 2059w, 2015s, 1998ms, 1625w	24.6(25.0)	1.2(1.3)
$n\text{-C}_3\text{H}_7$	3	61	68–72	2130w, 2059w, 2014s, 1998ms, 1624w	27.1(27.2)	1.7(1.8)
$n\text{-C}_4\text{H}_9$	4	65	70–73	2130w, 2058w, 2015s, 1998ms, 1622w	29.1(29.2)	2.3(2.2)
$n\text{-C}_5\text{H}_{11}$	5	62	62–64	2130w, 2059w, 2015s, 1998ms, 1620w	31.4(31.1)	2.6(2.6)
$n\text{-C}_6\text{H}_{13}$	6	71	53–56	2129w, 2058w, 2014s, 1998ms, 1622w	32.5(32.8)	2.8(3.0)
$n\text{-C}_7\text{H}_{15}$	7	58	49–53	2129w, 2059w, 2014s, 1998ms, 1625w	34.1(34.4)	3.1(3.3)
$n\text{-C}_8\text{H}_{17}$	8	60	48–51	2129w, 2058w, 2014s, 1998ms, 1624w	35.6(36.0)	3.4(3.7)
$n\text{-C}_9\text{H}_{19}$	9	72	43–47	2130w, 2059w, 2015s, 1999ms, 1615w	37.4(37.4)	3.9(4.0)
$n\text{-C}_{11}\text{H}_{23}$	10	74	42–45	2129w, 2058w, 2014s, 1998ms, 1625w	40.2(40.1)	4.5(4.6)
$n\text{-C}_{13}\text{H}_{27}$	11	67	50–53	2129w, 2058w, 2014s, 1998ms, 1625w	42.6(42.5)	5.2(5.1)
$n\text{-C}_{15}\text{H}_{31}$	12	65	60–62	2129w, 2059w, 2014s, 1998ms, 1622w	44.5(44.6)	5.3(5.5)
$n\text{-C}_{17}\text{H}_{35}$	13	74	61–63	2129w, 2058w, 2014s, 1998ms, 1624w	46.4(46.5)	5.9(5.9)

^a In hexane, w = weak, ms = medium/strong, s = strong.^b Sublimed first at 64°C.

The dimer (1.258 g, 1.122 mmol) was added to potassium (0.219 g) in THF (30 ml). The solution was refluxed under N_2 for ca. 48 h, after which the IR spectrum showed that a considerable amount of the anion $[\text{Re}(\text{CO})_4(\text{PPh}_3)]^-$ was present. The solution was syringed off under N_2 and added to heptanoyl chloride (0.34 g, 2.28 mmol) at 0°C. After 1.5 h of stirring at 0°C and then 2 h at room temperature, the solvent was removed under reduced pressure to give an orange oil, which was extracted with CH_2Cl_2 (ca. 20 ml). The extract was chromatographed on an alumina column made up with 50% CH_2Cl_2 /hexane. The product was eluted (with 50% CH_2Cl_2 /hexane) in the first (orange) band and removal of the solvent under reduced pressure gave an orange oil. Recrystallization from CH_2Cl_2 /hexane gave the product as yellow crystals in 20% yield. IR $\nu(\text{CO})$ in CH_2Cl_2 : 2080 (w), 1967 (m,br) and 1586 (w) cm^{-1} . ^1H NMR in CDCl_3 : δ 0.89 (c, 3H, CH_3); 1.20 (c, 6H, $(\text{CH}_2)_3\text{CH}_3$); 1.31 (c, 2H, Re-

COCH_2CH_2); 2.48 (c, 2H, ReCOCH_2); 7.45 (c, 15H, C_6H_5).

2.7. Attempted decarbonylation of *cis*- $[\text{Re}\{\text{CO}(n\text{-C}_6\text{H}_{13})\}(\text{CO})_4(\text{PPh}_3)]$

A solution of *cis*- $[\text{Re}\{\text{CO}(n\text{-C}_6\text{H}_{13})\}(\text{CO})_4(\text{PPh}_3)]$ (0.108 g; 0.160 mmol) in toluene (4.0 ml) was kept in a constant temperature bath at 94°C. IR spectra were recorded periodically and showed that no reaction occurred up to 48 h (ca. five half-lives for the reaction of PPh_3 with $[\text{Re}(n\text{-C}_6\text{H}_{13})(\text{CO})_5]$).

3. Results

3.1. Acyl compounds

The acyl compounds $[\text{Re}(\text{COCH}_3)(\text{CO})_5]$, **1**, [7] and $[\text{Re}(\text{COC}_2\text{H}_5)(\text{CO})_5]$, **2**, [8] have been reported previ-

Table 2
 ^1H NMR data for $[\text{Re}(\text{COR})(\text{CO})_5]$ ^a

R	Compound no.	ReCOCH_2	$\text{ReCOCH}_2\text{CH}_2$	$\text{ReCOCH}_2\text{CH}_2(\text{CH}_2)_n$	CH_3
CH_3	1				2.53s
C_2H_5	2	2.70q(2H)			0.87tr(3H)
$n\text{-C}_3\text{H}_7$	3	2.65tr(2H)	1.44q(2H)		0.83tr(3H)
$n\text{-C}_4\text{H}_9$	4	2.68tr(2H)	1.40q(2H)	1.22q(2H)	0.85tr(3H)
$n\text{-C}_5\text{H}_{11}$	5	2.62tr(2H)	1.49c(2H)	1.20c(4H)	0.81tr(3H)
$n\text{-C}_6\text{H}_{13}$	6	2.68tr(2H)	1.42c(2H)	1.22c(6H)	0.84tr(3H)
$n\text{-C}_7\text{H}_{15}$	7	2.69tr(2H)	1.44c(2H)	1.24c(8H)	0.85tr(3H)
$n\text{-C}_8\text{H}_{17}$	8	2.69tr(2H)	1.44c(2H)	1.24c(10H)	0.85tr(3H)
$n\text{-C}_9\text{H}_{19}$	9	2.70tr(2H)	1.46c(2H)	1.24c(12H)	0.86tr(3H)
$n\text{-C}_{11}\text{H}_{23}$	10	2.66tr(2H)	1.40c(2H)	1.17c(16H)	0.81tr(3H)
$n\text{-C}_{13}\text{H}_{27}$	11	2.64tr(2H)	1.41c(2H)	1.18c(20H)	0.81tr(3H)
$n\text{-C}_{15}\text{H}_{31}$	12	2.69tr(2H)	1.44c(2H)	1.24c(24H)	0.87tr(3H)
$n\text{-C}_{17}\text{H}_{35}$	13	2.70tr(2H)	1.43c(2H)	1.24c(28H)	0.87tr(3H)

^a In CDCl_3 relative to TMS (δ = 0.00 ppm), s = singlet, tr = triplet, q = quartet, c = complex signal.

Table 3
¹³C NMR data for [Re(CORX(CO))₅]^a

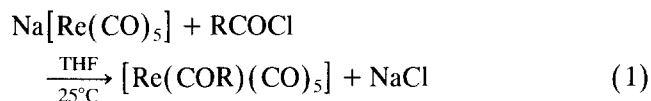
R	Compound no.	ReCO (acyl)	ReCO (cis) ^b	ReCO (trans) ^b	Re-COCH ₂	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇
CH ₃	1	245.0	182.9	181.1	57.4																
C ₂ H ₅	2	246.9	183.4	181.3	64.0	8.2															
n-C ₃ H ₇	3	247.2	183.5	181.4	72.8	17.2	13.5														
n-C ₄ H ₉	4	247.3	183.5	181.4	70.5	25.9	22.1	13.9													
n-C ₅ H ₁₁	5	247.6	183.4	181.4	70.8	31.2	23.5	22.6	13.9												
n-C ₆ H ₁₃	6	247.5	183.5	181.4	70.9	31.8	28.7	23.8	22.5	14.0											
n-C ₇ H ₁₅	7	247.3	183.3	181.2	70.7	31.5	29.0	28.8	23.6	22.4	13.8										
n-C ₈ H ₁₇	8	247.6	183.4	181.3	70.8	31.7	29.5	29.1	29.0	23.8	22.5	14.0									
n-C ₉ H ₁₉	9	247.4	183.3	181.2	70.7	31.7	29.4	29.3	29.1	28.0	23.6	22.5	13.9								
n-C ₁₁ H ₂₃	10	247.8	183.4	181.4	70.8	31.9	{29.6	→	→	→	→	28.8}°	23.8	22.6	14.0						
n-C ₁₃ H ₂₇	11	248.3	183.4	181.4	70.8	31.9	{29.6	→	→	→	→	28.9}°	23.9	22.7	14.1						
n-C ₁₅ H ₃₁	12	248.3	184.2	182.1	71.6	32.6	{30.4	→	→	→	→	29.8}°	24.5	23.4	14.8						
n-C ₁₇ H ₃₅	13	248.1	184.2	182.0	71.6	32.6	{30.4	→	→	→	→	29.8}°	26.38	24.5	23.4	14.8					

^a In CDCl₃ relative to TMS (δ = 0.00 ppm).

^b Relative to the alkyl chain.

^c Peaks were not resolved.

ously. We have now synthesized the new compounds $[\text{Re}(\text{COR})(\text{CO})_5]$ ($\text{R} = n\text{-C}_3\text{H}_7$ to $n\text{-C}_9\text{H}_{19}$; $n\text{-C}_{11}\text{H}_{23}$; $n\text{-C}_{13}\text{H}_{27}$; $n\text{-C}_{15}\text{H}_{31}$; $n\text{-C}_{17}\text{H}_{35}$) **3–13** by the reaction of $\text{Na}[\text{Re}(\text{CO})_5]$ with the appropriate acyl chloride (eqn. 1). Compounds **1** and **2** were also prepared in the same way.



All the compounds were isolated as pale-yellow microcrystalline solids which are stable in air in closed containers. They are also fairly stable in solution when kept under nitrogen. They have been fully characterized by melting point, microanalysis, and IR (Table 1), ^1H NMR (Table 2), ^{13}C NMR (Table 3) and mass spectrometry.

3.1.1. IR spectra

The IR spectra in the $\nu(\text{CO})$ region are in good agreement with the reported spectrum for $[\text{Re}(\text{COCH}_3)(\text{CO})_5]$ [7] and show the expected number of peaks for $[\text{M}(\text{COR})(\text{CO})_5]$ compounds [22] viz. A_1 (2130 cm^{-1}), B (2059 cm^{-1}), E (2014 cm^{-1}), A_1 (1998 cm^{-1}) and acyl (1622 cm^{-1}). It is noteworthy that all of these peaks appear at positions several wavenumbers higher than those for the analogous $[\text{Mn}(\text{COR})(\text{CO})_5]$ system [3]. This effect, i.e. a significant increase in $\nu(\text{CO})$ upon descending a Group in the Periodic Table has been observed previously for the $[\text{CpM}(\text{CO})_2(\text{R})]$ system ($\text{M} = \text{Fe}$ or Ru) [1]. There is no significant variation in $\nu(\text{CO})$ with change in the length of the alkyl chain.

3.1.2. NMR spectra

From the ^1H NMR data it can be seen that separate resonances are observed for the methyl protons and the α and β protons in these acyl compounds. The remaining methylene protons appear as a complex signal or a broad singlet. Once again, it is noteworthy that there is a significant downfield shift for the α protons in $[\text{Re}(\text{COR})(\text{CO})_5]$ cf. $[\text{Mn}(\text{COR})(\text{CO})_5]$ [3]. There is no significant variation in chemical shift with variation in the length of the alkyl chain and so integration provides the only way of distinguishing between the compounds by use of ^1H NMR measurements. This was also the case for related alkyl iron and ruthenium compounds [1].

The assignments for the ^{13}C NMR spectra were made by comparison with data reported for $[\text{Re}(\text{COCH}_3)(\text{CO})_5]$ [23] and $[\text{Mn}(\text{COR})(\text{CO})_5]$ [3]. The carbonyl resonances (terminal and acyl) are at the expected positions and are independent of the alkyl chain length. For compounds **1–9** all the carbon atoms of the alkyl chain were assigned. For compounds **10–13**, the peaks from the central carbon atoms were not resolved, as is the case for substituted n -alkanes [1]. Thus, the influence that the metal has on the chemical shifts of carbon atoms in the alkyl chain diminishes along the chain, and is only really apparent at the α and β positions.

3.1.3. Mass spectra

The mass spectra of **1–13** are all similar. They all show parent molecular ions with the predominant fragmentation pathway involving sequential loss of carbonyl groups followed by sequential loss of methylene frag-

Table 4
Data for $[\text{Re}(\text{R})(\text{CO})_5]$

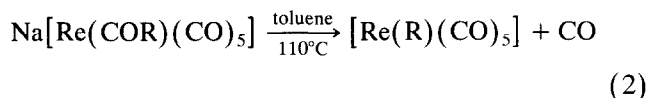
R	Compound no.	Yield (%)	M.P. ($^\circ\text{C}$)	IR $\nu(\text{CO})$ (cm^{-1}) ^a	Elemental analysis	
					C; found (calc.)	H; found (calc.)
C_2H_5	14	31	oil	2123(w), 2009(s), 1982(m)	23.2(23.7)	1.1(1.4)
$n\text{-C}_3\text{H}_7$	15	48	oil	2122(w), 2009(s), 1982(m)	25.8(26.0)	1.8(1.9)
$n\text{-C}_4\text{H}_9$	16	47	oil	2122(w), 2009(s), 1982(m)	28.0(28.2)	2.1(2.4)
$n\text{-C}_5\text{H}_{11}$	17	52	oil	2122(w), 2009(s), 1982(m)	30.4(30.2)	2.9(2.8)
$n\text{-C}_6\text{H}_{13}$	18	61	53–55	2123(w), 2009(s), 1982(m)	32.1(32.1)	3.1(3.2)
$n\text{-C}_7\text{H}_{15}$	19	38	54–57	2122(w), 2009(s), 1982(m)	33.7(33.9)	3.5(3.6)
$n\text{-C}_8\text{H}_{17}$	20	67	92–94	2122(w), 2009(s), 1982(m)	35.5(35.6)	3.8(3.9)
$n\text{-C}_9\text{H}_{19}$	21	71	26–29	2122(w), 2009(s), 1982(m)	37.4(37.1)	4.2(4.2)
$n\text{-C}_{10}\text{H}_{21}$	22	62	48–53	2122(w), 2009(s), 1982(m)	38.4(38.5)	4.4(4.5)
$n\text{-C}_{11}\text{H}_{23}$	23	74	28–30	2122(w), 2008(s), 1982(m)	39.7(39.9)	4.7(4.8)
$n\text{-C}_{12}\text{H}_{25}$	24	74	41–43	2122(w), 2009(s), 1982(m)	41.3(41.2)	5.1(5.1)
$n\text{-C}_{13}\text{H}_{27}$	25	82	29–31	2122(w), 2009(s), 1982(m)	42.5(42.4)	5.2(5.3)
$n\text{-C}_{14}\text{H}_{29}$	26	78	38–39	2122(w), 2009(s), 1982(m)	43.8(43.7)	5.4(5.6)
$n\text{-C}_{15}\text{H}_{31}$	27	74	30–32	2122(w), 2008(s), 1982(m)	44.5(44.7)	5.6(5.8)
$n\text{-C}_{16}\text{H}_{33}$	28	71	34–36	2122(w), 2009(s), 1982(m)	45.4(45.7)	6.1(6.0)
$n\text{-C}_{17}\text{H}_{35}$	29	80	32–34	2122(w), 2009(s), 1982(m)	46.4(46.5)	6.0(6.2)
$n\text{-C}_{18}\text{H}_{37}$	30	81	37–40	2122(w), 2009(s), 1982(m)	47.6(47.7)	6.5(6.4)

^a In hexane, w = weak, s = strong, m = medium.

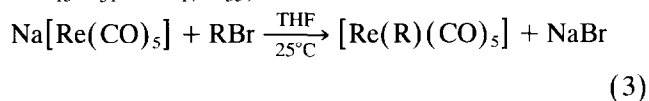
ments. The expected 37% ^{185}Re :63% ^{187}Re isotope distribution was seen for the rhenium-containing peaks.

3.2. Alkyl compounds

The alkyl compounds $[\text{Re}(\text{CH}_3)(\text{CO})_5]$ [7], $[\text{Re}(\text{C}_2\text{H}_5)(\text{CO})_5]$ [8] and $[\text{Re}(i\text{-Bu})(\text{CO})_5]$ [11] have been reported previously. Some substituted benzyl derivatives of rhenium pentacarbonyl, $[\text{Re}(\text{CH}_2\text{-C}_6\text{H}_4\text{X})(\text{CO})_5]$, are also known [12,15]. We have now synthesized and fully characterized the new *n*-alkyl compounds $[\text{Re}(\text{R})(\text{CO})_5]$ where R = *n*-propyl to *n*-octadecyl. Two synthetic methods were used, the first involving thermal decarbonylation of the acyl species, $[\text{Re}(\text{COR})(\text{CO})_5]$, as shown in Eqn. 2, and the second involving direct reaction of the rhenium pentacarbonyl anion with the appropriate *n*-alkyl bromide, as shown in Eqn. 3. The latter method was developed for certain R groups because the appropriate acyl chlorides were not readily available.



(R = C_2H_5 to $n\text{-C}_9\text{H}_{19}$; $n\text{-C}_{11}\text{H}_{23}$; $n\text{-C}_{13}\text{H}_{27}$; $n\text{-C}_{15}\text{H}_{31}$; $n\text{-C}_{17}\text{H}_{35}$)



(R = $\text{C}_{10}\text{H}_{21}$; $n\text{-C}_{12}\text{H}_{25}$; $n\text{-C}_{14}\text{H}_{29}$; $n\text{-C}_{16}\text{H}_{33}$; $n\text{-C}_{18}\text{H}_{37}$)

All the compounds were isolated as either yellow oils or pale-yellow solids. They are stable thermally and to air.

They have been fully characterized by melting point, microanalysis, IR (Table 4), ^1H NMR (Table 5), ^{13}C NMR (Table 6) and mass spectrometry.

The fact that the $[\text{Re}(\text{C}_2\text{H}_5)(\text{CO})_5]$ we made was fairly stable (it does not decompose when kept under nitrogen at 0°C for several months) is further evidence that ethylmanganese pentacarbonyl (which is notoriously unstable) does not decompose by β -hydride elimination. We have previously suggested that the decomposition mechanism of $[\text{Mn}(\text{C}_2\text{H}_5)(\text{CO})_5]$ involves a very rapid ethyl migration/carbonylation process [3]. Ethylrhenium pentacarbonyl contains β -hydrogens and yet is relatively stable; it is known that $[\text{Re}(\text{R})(\text{CO})_5]$ species undergo alkyl migration to form CO-inserted products more slowly than do $[\text{Mn}(\text{R})(\text{CO})_5]$ compounds [18], which perhaps is largely because of a much stronger metal–carbon bond [19]. A likely reason for the increased stability of $[\text{Re}(\text{C}_2\text{H}_5)(\text{CO})_5]$ over $[\text{Mn}(\text{C}_2\text{H}_5)(\text{CO})_5]$ is thus that the rhenium compound undergoes the alkyl migration/carbonylation reaction more slowly than does the analogous manganese compound.

3.2.1. IR spectra

The IR spectra in the $\nu(\text{CO})$ region show the expected number of peaks for $[\text{Mn}(\text{R})(\text{CO})_5]$ species, viz. A_1 (2112 cm^{-1}), E (2009 cm^{-1}) and A_1 (1982 cm^{-1}). Again, the wavenumbers were higher than for the analogous $[\text{Mn}(\text{R})(\text{CO})_5]$ compounds. There was no detectable variation in $\nu(\text{CO})$ upon change in the length of the alkyl chain. The data are in good agreement with those reported for $[\text{Re}(\text{CH}_3)(\text{CO})_5]$ [7] and $[\text{Re}(\text{C}_2\text{H}_5)(\text{CO})_5]$ [8].

Table 5
 ^1H NMR data for $[\text{Re}(\text{R})(\text{CO})_5]^a$

R	Compound no.	ReCH_2	ReCH_2CH_2	$\text{ReCH}_2\text{CH}_2(\text{CH}_2)_x$	CH_3
C_2H_5	14	1.01(q,2H)			1.75(tr,3H)
$n\text{-C}_3\text{H}_7$	15	0.95(tr,2H)	1.80(m,2H)		0.95(tr,3H)
$n\text{-C}_4\text{H}_9$	16	0.93(m,2H)	1.79(m,2H)	1.30(brs,2H)	0.90(tr,3H)
$n\text{-C}_5\text{H}_{11}$	17	0.93(m,2H)	1.78(m,2H)	1.30(brs,4H)	0.90(tr,3H)
$n\text{-C}_6\text{H}_{13}$	18	0.93(m,2H)	1.78(m,2H)	1.30(brs,6H)	0.90(tr,3H)
$n\text{-C}_7\text{H}_{15}$	19	0.97(m,2H)	1.78(m,2H)	1.26(brs,8H)	0.86(tr,3H)
$n\text{-C}_8\text{H}_{17}$	20	0.98(m,2H)	1.82(m,2H)	1.28(brs,10H)	0.89(tr,3H)
$n\text{-C}_9\text{H}_{19}$	21	0.96(m,2H)	1.79(m,2H)	1.22(brs,12H)	0.83(tr,3H)
$n\text{-C}_{10}\text{H}_{21}$	22	0.92(m,2H)	1.70(m,2H)	1.21(brs,14H)	0.81(tr,3H)
$n\text{-C}_{11}\text{H}_{23}$	23	0.92(m,2H)	1.74(m,2H)	1.30(brs,16H)	0.86(tr,3H)
$n\text{-C}_{12}\text{H}_{25}$	24	0.95(m,2H)	1.74(m,2H)	1.24(brs,18H)	0.85(tr,3H)
$n\text{-C}_{13}\text{H}_{27}$	25	0.93(m,2H)	1.75(m,2H)	1.28(brs,20H)	0.85(tr,3H)
$n\text{-C}_{14}\text{H}_{29}$	26	0.92(m,2H)	1.72(m,2H)	1.21(brs,22H)	0.84(tr,3H)
$n\text{-C}_{15}\text{H}_{31}$	27	0.95(m,2H)	1.77(m,2H)	1.27(brs,24H)	0.86(tr,3H)
$n\text{-C}_{16}\text{H}_{33}$	28	0.96(m,2H)	1.73(m,2H)	1.27(brs,26H)	0.87(tr,3H)
$n\text{-C}_{17}\text{H}_{35}$	29	0.96(m,2H)	1.77(m,2H)	1.25(brs,28H)	0.88(tr,3H)
$n\text{-C}_{18}\text{H}_{37}$	30	0.95(m,2H)	1.80(m,2H)	1.24(brs,30H)	0.87(tr,3H)

^a In CDCl_3 relative to TMS ($\delta = 0.00$ ppm), q = quartet, tr = triplet, m = complex multiplet, brs = broad singlet.

Table 6
¹³C NMR data for [Re(R)(CO)₃]^a

R	Com- pound	CO (<i>cis</i>) ^b	CO (<i>trans</i>) ^b	ReCH ₂ i.e. C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇	C ₁₈
C ₂ H ₅	14	186.07	181.52	1.03	22.88																
<i>n</i> -C ₃ H ₇	15	186.02	181.50	-6.20	32.24	21.98															
<i>n</i> -C ₄ H ₉	16	186.04	181.48	-9.46	41.45	30.30	13.51														
<i>n</i> -C ₅ H ₁₁	17	186.06	181.48	-9.17	39.61	38.76	22.14	14.14													
<i>n</i> -C ₆ H ₁₃	18	185.51	180.90	-9.65	38.58	36.54	30.86	22.22	13.55												
<i>n</i> -C ₇ H ₁₅	19	186.04	181.47	-9.38	39.29	36.81	31.23	29.10	22.34	14.10											
<i>n</i> -C ₈ H ₁₇	20	186.05	181.46	-9.09	39.17	37.44	31.75	29.43	29.11	22.69	14.08										
<i>n</i> -C ₉ H ₁₉	21	186.05	181.43	-9.13	39.20	37.39	31.82	29.61	29.34	29.29	22.68	14.13									
<i>n</i> -C ₁₀ H ₂₁	22	186.05	181.49	-9.08	39.19	37.46	31.94	29.78	29.71	29.37	22.70	14.11									
<i>n</i> -C ₁₁ H ₂₃	23	186.10	181.51	-9.20	39.18	37.51	31.94	{29.77				22.67	13.99								
<i>n</i> -C ₁₂ H ₂₅	24	186.04	181.49	-9.08	39.19	37.46	31.94	{29.78				29.37} ^c	22.70	14.10							
<i>n</i> -C ₁₃ H ₂₇	25	186.21	181.40	-9.13	39.13	37.44	31.94	{29.76				29.34} ^c	22.71	14.04							
<i>n</i> -C ₁₄ H ₂₉	26	185.83	181.26	-9.28	38.99	37.26	31.89	{29.58				29.17} ^c	22.49	13.88							
<i>n</i> -C ₁₅ H ₃₁	27	186.10	181.22	-9.21	38.97	37.29	31.70	{29.61				29.20} ^c	22.64	14.12							
<i>n</i> -C ₁₆ H ₃₃	28	185.83	181.22	-9.29	38.98	37.25	31.73	{29.50				29.16} ^c	22.49	13.89							
<i>n</i> -C ₁₇ H ₃₅	29	186.05	181.20	-8.98	39.19	37.46	31.94	{29.71				29.17} ^c	22.70	14.11							
<i>n</i> -C ₁₈ H ₃₇	30	185.96	181.14	-9.11	39.10	37.38	31.85	{29.62				29.28} ^c	22.61	14.02							

^a In CDCl₃ relative to TMS (δ = 0.00 ppm).

^b Relative to the alkyl chain.

^c Peaks were not resolved.

3.2.2. NMR spectra

From the ^1H NMR data, it can be seen that separate resonances are observed for the methyl protons and the α and β protons for the alkyl chain. The remaining methylene protons appear as a broad singlet. The α protons of the alkyl chain resonate at a very similar position to those of the methyl protons; in fact, for $[\text{Re}(\text{CH}_2\text{CH}_2\text{CH}_3)(\text{CO})_5]$, these two resonances are superimposed i.e. the methyl and α protons are “equivalent” in this case. This behaviour is a result of the strong shielding effect of the rhenium atom, and is also observed in the ^{13}C NMR spectra. There was no detectable variation in chemical shift on change in the length of the alkyl chain.

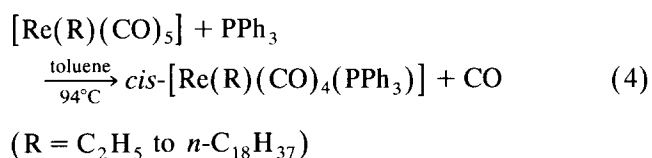
The ^{13}C NMR data are given in Table 6. The carbonyl resonances are at the expected positions and are independent of alkyl chain length. The signal at ca. -9.2 ppm was assigned to the α carbon atom of the alkyl chain, and the shift shows that the metal atom is exerting a very strong shielding effect. For compounds **14–22** (i.e. $\text{R} = \text{ethyl to } n\text{-decyl}$), separate resonances are observed for all of the carbon atoms of the alkyl chain. For compounds **23–30** ($\text{R} = n\text{-undecyl to } n\text{-octadecyl}$), the peaks from the central methylene carbon atoms were not resolved, as was the case for substituted n -alkanes and related long chain alkyl complexes of manganese [3], iron and ruthenium [1]. The effects of the metal are only noticeable on the first two carbon atoms of the alkyl chain.

3.2.3. Mass spectra

The mass spectra for compounds **15–30** are all similar and relatively simple. Parent molecular ions were not seen for any of the compounds, but the highest mass peak for all compounds corresponded to $\text{M}-2\text{CO}$. The major fragmentation pathway was then loss of the other carbonyl groups followed by sequential loss of methylene fragments.

3.3. Reactivity studies

The reaction of $[\text{Re}(\text{R})(\text{CO})_5]$ with triphenylphosphine (Eqn. 4) was monitored by IR spectroscopy.



The products were characterized as follows. Typically, $\nu(\text{CO})$ in CH_2Cl_2 at ca. 2023 cm^{-1} (weak), 1954 cm^{-1} (shoulder), 1927 cm^{-1} (strong) and ^1H NMR (in CDCl_3 ; $\delta = \text{ca. } 0.8$ ppm) (broad triplet, 3H) CH_3 ; 0.9 ppm (complex, 2H) ReCH_2 ; 1.25 ppm (broad singlet) $(\text{CH}_2)_x$ and 7.4 ppm (complex, 15 H) PPh_3 . The same type of product was obtained for all the R groups.

It was established that the reactions went to completion, but reliable rate data were not obtained. The use of toluene as a solvent resulted in broad peaks in the IR spectra giving unreliable intensity readings. High temperatures and long reaction times (relative to those used for the manganese system) may also lead to side reactions.

4. Discussion

We have synthesized and characterized an extensive homologous series of new alkyl and acyl complexes of rhenium of the types $[\text{Re}(\text{R})(\text{CO})_5]$ and $[\text{Re}(\text{COR})(\text{CO})_5]$. These complexes, including the ethyl derivative $[\text{Re}(\text{C}_2\text{H}_5)(\text{CO})_5]$, were all fairly stable, both thermally and to air. No evidence that $[\text{Re}(\text{C}_2\text{H}_5)(\text{CO})_5]$ undergoes a carbonylation reaction was obtained. Thus, $[\text{Re}(\text{C}_2\text{H}_5)(\text{CO})_5]$ is significantly more stable than $[\text{Mn}(\text{C}_2\text{H}_5)(\text{CO})_5]$. This is probably because of the fact that the rhenium–carbon bond is stronger than the manganese–carbon bond [19].

It was established that the reactions of $[\text{Re}(\text{R})(\text{CO})_5]$ with PPh_3 went to completion to form the products $\text{cis}-[\text{Re}(\text{R})(\text{CO})_4(\text{PPh}_3)]$, but reliable rate data were not obtained. However, the following facts were established:

(i) The rates of the reactions of $[\text{Re}(\text{R})(\text{CO})_5]$ with PPh_3 were considerably slower than those for the analogous manganese complexes.

(ii) Only a very slight dependence of reaction rate on alkyl chain length was observed.

(iii) This dependence followed the same general pattern as that for the $[\text{Mn}(\text{R})(\text{CO})_5]$ system, [3], i.e. the rate increased initially for the SCA groups and then decreased with increasing size of the alkyl chain.

(iv) Estimates of rate constants gave values in the range $0.1(5) \times 10^{-4}\text{ s}^{-1}$ (for $\text{R} = \text{C}_2\text{H}_5$) to $0.3 \times 10^{-4}\text{ s}^{-1}$ (for $\text{R} = n\text{-C}_8\text{H}_{17}$). These rate constants span a much narrower range than those determined for the $[\text{Mn}(\text{R})(\text{CO})_5]$ system [3].

(v) The compound $\text{cis}-[\text{Re}(\text{CO}(n\text{-C}_6\text{H}_{13}))(\text{CO})_4(\text{PPh}_3)]$ underwent no detectable decarbonylation at 94°C , not even in a period equivalent to five half-lives for the reaction of $[\text{Re}(n\text{-C}_6\text{H}_{13})(\text{CO})_5]$. Thus, we do not believe that the reaction of $[\text{Re}(\text{R})(\text{CO})_5]$ with PPh_3 to give the products $\text{cis}-[\text{Re}(\text{R})(\text{CO})_4(\text{PPh}_3)]$ proceeds via the intermediate formation of $\text{cis}-[\text{Re}(\text{COR})(\text{CO})_4(\text{PPh}_3)]$.

(vi) No evidence was obtained for formation of acyl species in the course of the reactions. This, in addition to (ii) and (v) above, indicates that the reaction of $[\text{Re}(\text{R})(\text{CO})_5]$ compounds with PPh_3 is a simple substitution reaction in which a terminal carbonyl group is replaced by PPh_3 , a process that probably involves initial loss of a terminal carbonyl group.

The manganese and rhenium alkyl compounds gave different types of products on reaction with PPh_3 , largely, we suggest, because of the much greater strength of the rhenium–carbon (alkyl) bond than of the manganese–carbon(alkyl) bond (i.e. $222.6 \text{ kJ mol}^{-1}$ for Re-CH_3 in $[\text{Re}(\text{CH}_3)(\text{CO})_5]$ and $116.1 \text{ kJ mol}^{-1}$ for Mn-CH_3 in $[\text{Mn}(\text{CH}_3)(\text{CO})_5]$ [19]). This difference results in the two systems following two different reaction pathways, which is supported by the relative independence of the rate on the nature of the alkyl group in $[\text{Re}(\text{R})(\text{CO})_5]$. For the $[\text{Mn}(\text{R})(\text{CO})_5]$ system, the products from reaction with PPh_3 were, in all cases, *cis*- $[\text{Mn}(\text{COR})(\text{CO})_4(\text{PPh}_3)]$ ($\text{R} = \text{CH}_3$ to $n\text{-C}_{18}\text{H}_{37}$) [3].

Acknowledgements

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References

- [1] A. Emeran, M.A. Gafoor, J.K.I. Goslett, Y.-H. Liao, L. Pimble and J.R. Moss, *J. Organomet. Chem.*, **405** (1991) 237.
- [2] J. Andersen and J.R. Moss, *J. Organomet. Chem.*, **439** (1992) C25.
- [3] J. Andersen and J.R. Moss, *Organometallics*, **13** (1994) 5013.
- [4] J.N. Cawse, R.A. Fiato and R.L. Pruett, *J. Organomet. Chem.*, **172** (1979) 405.
- [5] B.J. Burger, M.E. Thompson, W.D. Cotter and J.E. Bercaw, *J. Am. Chem. Soc.*, **112** (1990) 1566.
- [6] H. Berke and R. Hoffman, *J. Am. Chem. Soc.*, **100** (1978) 7224.
- [7] W. Hieber, G. Braun and W. Beck, *Chem. Ber.*, **93** (1960) 901.
- [8] A. Davison, J.A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, (1963) 1133.
- [9] E.O. Fischer and K. Fichtel, *Chem. Ber.*, **94** (1961) 1200; A.M. Brodie, G. Hulley, B.F.G. Johnson and J. Lewis, *J. Organomet. Chem.*, **24** (1970) 201.
- [10] K. Raab, U. Nagel and W. Beck, *Z. Naturforsch.*, **38b** (1983) 1466.
- [11] K.E. Warner and J.R. Norton, *Organometallics*, **4** (1985) 2250.
- [12] T.L. Bent, S.R. Clarkson, J.D. Cotton and R.D. Markwell, *Proc. XXVIII Int. Conf. Coord. Chem.*, Gold Coast, Australia, 1989, paper M24.
- [13] A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and A.A. Ioganson, *Dokl. Akad. Nauk. SSSR*, **175** (1967) 1293.
- [14] A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and A.A. Ioganson, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1968) 1892.
- [15] A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and A.A. Ioganson, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1968) 395.
- [16] J.M. Andersen and J.R. Moss, *Advances in Organometallic Chemistry*, **37** (1995) 169.
- [17] A. Wojcicki, *Adv. Organomet. Chem.*, **11** (1973) 87.
- [18] F. Calderazzo, *Angew. Chem., Int. Edn. Engl.*, **16** (1977) 299.
- [19] D.L.S. Brown, J.A. Connor and H.A. Skinner, *J. Organomet. Chem.*, **81** (1974) 403.
- [20] T. Ziegler, V. Tschinke and A. Becke, *J. Am. Chem. Soc.*, **109** (1987) 1351.
- [21] D.G. Dewit, J.P. Fawcett and A. Poe, *J. Chem. Soc., Dalton Trans.*, (1976) 528.
- [22] L.E. Orgel, *Inorg. Chem.*, **1** (1962) 25.
- [23] M.J. Webb and W.A.G. Graham, *J. Organomet. Chem.*, **93** (1975) 119.