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PREPARATIVE STUDIES OF ALKOXY DERIVATIVES OF MANGANESE CARBONYL

by

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A thesis submitted to the University of Durham
for the degree of Master of Science

September 1988

Declaration

The work in this thesis was carried out in the University of Durham between September 1987 and June 1988. It has not been submitted, either wholly or in part, for a degree in this or any other University and is the original work of the author except where acknowledged by reference.

Acknowledgements

I wish to express my appreciation to my supervisor Dr. M. Kilner for his advice and encouragement during this period of study. My thanks also to Miss J.M. Magee for her advice with regards to experimental proceedures.

I am indebted to my parents for their support and generosity which made this work possible.

G. Bell

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Preparative Studies of Alkoxy Derivatives of Manganese Carbonyl

Abstract

Oligomeric alkoxy derivatives of bromopentacarbonyl manganese (I) and bromotetracarbonylmanganese[+](I) were prepared by reaction with a base and a variety of alcohols. The nature of the products, their structural and bonding features are discussed in the context of alkoxide chemistry in general.

Reactions of $Mn(CO)_5Br$ with triethylamine and alcohols in hydrocarbon solvents at 55°C were monitored by IR spectroscopy which indicated the formation of one major product, either a $Mn_3(CO)_9(OR)_3$ or a $Mn_4(CO)_{12}(OR)_4$ complex. Yields were non-reproducible and isolated solids were shown to be a mixture of products. Mass spectral data indicated oligomers of the type $[Mn(CO)_3(OR)]_n$, where n = 3 to 6, and dimers of formula $[Mn(CO)_4(OR)]_2$. Reliable yields were obtained using sodium carbonate as the base and acetone as the solvent. The products are mixtures and mass spectral data shows a predominance of trimeric alkoxy derivatives, although products with n = 4 to 6 and dimers were also found. A monomer was obtained with triphenylcarbinol, $Mn(CO)_5(OCPh_3)$.

The results of the reactions of $Mn(CO)_4(PPh_3)Br$ with triethylamine and alcohols in hydrocarbon solvents are more difficult to interpret. Mixtures of products are obtained, dimeric alkoxy derivatives $[Mn(CO)_3(PPh_3)OR]_2$ predominating. However, non-alkoxy complexes appear to be the major products in a number of cases.

A 1.2ppm shift in the d_6-acetone ^1H NMR spectrum of the methoxy complex $[Mn(CO)_3(OMe)]_n$ was attributed to paramagnetic species of the type $[Mn(OMe)_2]_n$. These paramagnetic compounds may well be present in other product mixtures.

Attempted purification techniques and methods of separation of the product mixtures are also discussed.

[+] ERRATUM

For 'bromotetracarbonyl manganese(I)' read

'bromotetracarbonyl(triphenylphosphine) manganese(I)'

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Chapter 4

Section I

Section II

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CHAPTER 1

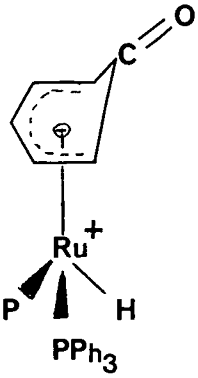
INTRODUCTION

As early as 1846 alkoxy derivatives of silicon and boron were described [1,2] but the tetraethoxide of titanium was not synthesised until 1924 by Bischoff and Adkins [3]. Thereafter development of alkoxide chemistry was slow until the 1950's. Up to this time only isolated alkoxides of the first row transition metals were reported [4-8], but following the synthesis of zirconium ethoxide by Bradley and Wardlaw in 1950 [9], work on the alkoxides has developed rapidly. In the last two decades a wealth of publications have dealt with simple alkoxides, alkoxy derivatives and, more recently, detailed studies using sterically hindered alcohols for enhancing the kinetic stability of transition metal alkoxides in general, and the generation of bimetallic, or double, alkoxides. Important developments in the knowledge of alkoxide chemistry have occurred with the determination of crystal structures, magnetic and spectroscopic properties, and thermochemical measurements. Simple alkoxides are known for almost all the transition metals and present research is concentrated on preparing novel alkoxy derivatives and developing their uses. Of the transition metals, only technetium and silver have no known alkoxy compounds at present.

In general, the main focus of attention has been on the early transition metals, up to and including the chromium group, with the exception of Winter's work on the electronic and magnetochemistry of the simple alkoxides of the later metals [10]. The simple alkoxides of the early transition metals are soluble and volatile in contrast to the insoluble and non-volatile compounds of the later metals (with the exception of $Cr(OR^t)_4$ and $Fe(OR)_3$), which have also been found to be less reactive towards other alcohols and reactivity is more selective, both reasons being offered for their lack of study until recently. A major difficulty in the study of alkoxides has been their air and moisture sensitivity (manganese and chromium alkoxides can be pyrophoric on exposure to air [11,12]) which hampered early research workers and still poses some problems to their study.

Defining an Alkoxide

Binary metal alkoxides have the general formula $M(OR)_x$ and can be considered to be derivatives of alcohols (ROH) in which the hydroxylic hydrogen has been replaced by a metal (M). These compounds involve $\overset{\delta+}{M}-\overset{\delta-}{O}-C$ bonds, polarized in the manner indicated due to the high electronegativity of oxygen, the degree of polarization depending upon the electronegativity of the metal, M. For derivatives of the same element the covalent character of the M-O bond increases with greater inductive effect of the alkyl group; for example, among the isomeric butoxides of an element the tertiary butoxide should have the highest covalent character. The polarity of the M-O bond may also be partially offset in cases of electrophilic metals, which undergo covalency expansion by intermolecular coordination through the oxygen atoms of the alkoxy groups. This type of molecular association appears to be sensitive to steric factors, such as the bulk of the alkyl group [13]. This bridging facility leads to coordination polymerization and the formation of oligomeric species e.g. $[M(OR)_x]_n$ and $[Mn(CO)_3(OR)]_n$. Phenoxide can also act as a bridging ligand as in the complex $(PhO)Cl_2Ti-\mu(OPh)_2TiCl_2(OPh)$, which contains OPh as terminal (unidentate) and bridging ligands. With phenoxide a third possibility is also evident, that is the ligand can be bound to the metals as in:

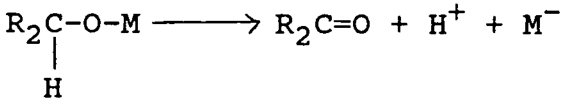


The alkoxy group can also function as a bridging group between different metal atoms which gives rise to bimetallic alkoxides of the type:

$(RO)_{n-2}M[Al(OR)_4]_2$ where M = Zr, Hf, Nb or Ta.

Despite the strong metal-oxygen bonds, another characteristic property of the metal alkoxides is their lability, especially among the early transition metals, due to facile OR group exchange (both intra- and intermolecular) which has been the subject of a number of NMR studies [15]. This property has been used extensively for the synthesis of higher alkoxides and other derivatives, for example, products from the reaction of the metal alkoxide with glycols, β-diketones, alkanolamines, oximes and Schiff bases [16-22].

Metal alkoxides having β-CH bonds can reduce transition metals by a hydride transfer pathway yielding aldehydes or ketones:



$$R_2\underset{\displaystyle H}{\underset{|}{C}}\text{-O-M} \longrightarrow R_2C{=}O + H^+ + M^-$$ [23]

Because of these redox, and also bridging, tendencies the alkoxide group was previously little used as an ancillary ligand for organometallic complexes which act as reagents or catalysts. However, this situation has changed rapidly, especially with the development of very sterically hindered alkoxide ligands such as tri-t-butyl methoxide (tritox), which has a steric core similar to a bulky phosphine. Remarkably thermally stable, unsaturated alkyls such as

$$(\text{tritox})_2\text{-M}(CH_3)_2 \qquad M = Ti,\ Zr$$

have been made.

This dual ability of alkoxide to form strong covalent bonds and to act as a bridging ligand have made it of considerable interest to chemists. Its bonding is also of interest as the alkoxy group is an important π donor ligand.

Bonding in Alkoxide Complexes

The development of organotransition metal chemistry has been with π acceptor ligands such as carbonyl, tertiary phosphines, olefins and cyclopentadienes, which are well suited to low-valent, d^n electron-rich metal centres [24]. Alkoxides, however, are an important class of π donor ligands, which also includes halides, amides, oxides and nitrides. π donors stabilize the high oxidation states of early transition metals, which are d^n electron poor [25]. Relatively little is known at present about their role in organometallic chemistry but several significant consequences of π donating ligands have been found, which include both structural and kinetic effects. π bonding may perturb d^n electrons, M-M bonding and the reactivity of other ligands bonded to the same metal centre.

Metal-Oxygen π-Bonding in Transition Metal Alkoxides [24]

A wealth of structural evidence has been collected for metal alkoxides which provides physical evidence for π bonding. Chisholm has estimated that a purely σ bonding Mo(III)-O distance for an Mo_2^{6+} centre should be approximately 2.06Å, which is typical of Mo-μ-OR distances, but considerably longer than any seen for terminal Mo-OR groups, which fall in the range 1.80-1.96Å [216]. These short Mo-O distances are strongly suggestive of a considerable amount of double-bond character in such systems. Shorter, terminal M-OR distances are associated with larger M-O-C angles which may be close to 180°. In contrast, relatively long terminal M-OR distances are associated with small M-O-C angles, typically in the range 120-130°.

Comparison of the bonding of alkoxide and aryloxide ligands to the same metal centre has shown that M-OAr distances are slightly longer than M-OR distances, but that the M-O-Ar angles are characteristically larger than the M-O-R angles, even in the absence of steric effects [27]. Angles of 160-180° are common for aryloxide ligands.

In most cases structural changes observed in M-O distances and M-O-C angles can be attribtued to oxygen interactions with the metal. Two electron donation from the alkoxide ligand to the metal can be supplemented by donation up to a maximum of π^4. Electron deficient metal centres commonly found for complexes of the early transition metals typically exhibit the short M-O distances and large M-O-C angles which imply a large degree of π bonding. Where there are no vacant d orbitals on the metals, or they are used in M-M bonding, the M-O distances approach those expected for single bonds and the M-O-C angles are close to 120°, as, for example, is found in $Mo_2(OR)_4$ compounds [28].

The extreme flexibility of the M-O-C angles of aryloxides can be accounted for by π interactions. The aryl group can form π bonds with oxygen, and a competition for the electron density on oxygen is established between the aryl group and the metal, which stabilizes the linear M-O-Ar moiety and reduces the relative π donation to the metal.

π donor effects of Alkoxides on neighbouring ligands

The influence of alkoxides' π donation on other ligands within a complex may be observed in their reactivity and their spectroscopic properties. Strong donor ligands can enhance back-bonding to π acid ligands, such as carbonyl or nitrosyl, on the same metal. The complexs $Mo(OBu^t)_2(py)_2(CO)_2$ and $Mo(OPr^i)_2(bipy)_2$ [29,30] are illustrative. The former has the anomalously low ν(CO) values of 1906 and 1776 cm^{-1} for a cis $(CO)_2Mo^{2+}$ compound, whilst in the latter the 2,2′ bipyridyl ligands are partially reduced. Both reflect the fact that RO-Mo π bonding has raised the energy of the $t^4{}_{2g}$ orbitals and thus enhances back-bonding to CO π^* and bipy π^* orbitals. In $W(OBu^t)_3(NO)(py)$ [31] extensive π back-bonding is evident from the extremely short W-NO distance and the exceedingly low value of ν(N-O), 1555 cm^{-1}, for a terminal NO ligand.

A more quantitative measure of the enhanced π back-bonding to adjacent ligands has been shown by Chisholm in a series of related compounds of formula $W_2(OBu^t)_6(\mu\text{-}CX)$ where X = O and NR [24]. A characteristic spectroscopic feature of the μCX ligand is the exceptionally low values of ν(CO) for a μ_2-CO moiety (1598cm^{-1}) and ν(C-N) for a μ_2-CNR moiety (1530 and 1525cm^{-1} when R = Bu^t and 2,6 dimethylphenyl respectively). These low values of ν(C-O) and ν(C-N) imply a large degree of reduction in the μ-CO and μ-CNR ligands. Investigations via Fenske-Hall calculations on model systems, indicate that the weakening of the C-X bonds can be attributed primarily to the degree of π back-bonding in the $M_2(\mu\text{-}CX)$ moiety.

This molecular orbital approach also provides an insight into likely modes of reactivity. For compounds with M-X bonds that are ligand centred, the π^* M.O.s will be low lying and metal centred, thus nucleophilic attack at the metal is a likely reaction mode, in addition to electrophilic attack on the ligand centred π-orbital. π-donation into filled metal d-orbitals or occupied M-M bonds will have a destabilising influence on the d^n electrons of the M-M bond. Oxidation is thus a likely reaction pathway.

Further examples of metal-oxygen π bonding and its effects on neighbouring ligands are to be found in Chapter 2.

The Present and Future of Alkoxide Chemistry

Current research has seen the synthesis of novel alkoxides such as alkenoxides, cinnamoxides, 3-pentene-2-oxides and 4-pentene-2-oxides, and β-methalloxides of titanium, niobium and tantalum using sterically hindered alcohols, and also numerous bimetallic alkoxides, work pioneered by Mehrotra [32]. There is a great deal of potential for further development here, as well as in understanding structure and bonding found in alkoxides due to their π donating abilities.

During the last sixty years an increasing number of industrial uses have been found for alkoxides. Their use depends on their chemical reactivity coupled with their volatility and solubility in common organic solvents. Their chemical reactivity leads to a variety of catalytic applications, ranging from olefin polymerization (titanium and vanadium alkoxides as components of Ziegler-Natta catalysts) to accelerators for the drying of paints and inks. They are also valuable precursors to the metal oxides through hydrolysis, pyrolysis or combustion. Where high purity is at stake the metal alkoxides offer considerable advantages in the preparation of metal oxides required in the microelectronics industry.

The alkoxides have a relationship with the metal oxides used in heterogeneous catalysis and they may provide a means of producing highly reactive forms of oxide catalysts.

Alkoxides are also models for species formed on oxide surfaces when, for example, hydrocarbons are oxidized. Another possible use is as precursors for ceramics and other new materials currently of great interest. Clearly, the possible uses and importance of alkoxides will increase to keep pace with the rapid developments in their numbers and variety.

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CHAPTER 2

A SURVEY OF SOME ALKOXY DERIVATIVES OF THE TRANSITION METALS

Introduction

This chapter reviews the preparation and reactions of alkoxy derivatives of the Transition Metals. For sake of completeness the Scandium and Zinc groups are included, although these are frequently not considered as typical transition elements in their reactions. The uses of these compounds are also considered.

A number of very good reviews of the subject exist which give greater detail of methods of preparation, chemical and physical properties, and reactions [1-8].

Scandium, Yittrium, and Lanthanum

Relatively little work has been carried out on this group as compared to the other transition metals, but more recently the considerable interest has arisen in the alkoxides of the lanthanides and actinides, which are beyond the scope of this review. These have been reviewed [9],together with the simple alkoxides [10].

$Cp_2Y(OMe)$ has been prepared, amongst a mixture of products,using $[Cp_2YCl(THF)]$ and potassium methoxide in THF. The same reaction using methanol as solvent at -78°C gives the methoxy compound as the major product, but at 30°C the product is $Cp_2Y_5(\mu_2\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)$, a minor product at the lower temperature [11].

Titanium, Zirconium, and Hafnium

A considerable amount of work has been published on the binary alkoxides of this group of metals, in particular those of titanium, whose largest and most intensively studied organic compounds are the alkoxides. One of the earliest attempted syntheses of a transition metal alkoxide was made by Demarcay in 1875 when he undertook the preparation of the tetraethoxide of titanium, although he in fact most likely made an alkoxy derivative $Ti(OEt)_2Cl_2.EtOH$ [5]. Details of the preparation and properties of the binary alkoxides can be found in refs. [3,4,12].

Alkoxy Derivatives

Alkoxy Metal Halides

The alkoxy halides of titanium have been prepared using two main methods: the partial replacement of halide from the tetrahalides or an existing alkoxy halide, and the partial replacement of alkoxy groups from the tetralkoxy compounds. Similarly with the zirconium analogues. For example:

$$TiCl_4 + ROH \longrightarrow TiCl_3(OR) + HCl$$

Good yields can be obtained using chloroform as the solvent and carrying out the reaction at 0°C. The R groups can be primary, secondary, or tertiary. A base is required to remove HCl to prevent hydrolysis of the product. Their insolubility indicates a polymeric nature and alkoxide bridges are indicated from IR studies. Tertiary and trialkyl alkoxy halides can also be prepared by transesterification reactions:

$$(EtO)_3TiCl + 3ROH \longrightarrow (RO)_3TiCl + 3EtOH$$

Mixed alkoxides can be obtained by reacting a $TiCl_2(OR)_2$ complex with an alcohol in the presence of pyridine.

Gianetti [13] has prepared $Ti(OR)_nCl_{3-n}$ complexes from $TiCl_3$ and trialkyl formate.

Nesmeyanov [14] obtained $TiCl_2(OR)_2$ by the second general method, reacting the tetralkoxide with chlorine gas. $TiCl_2(OBu^t)_2$ has been found to be dimeric and the Ti atom to be five coordinate [15]. Reaction also occurs with organic and inorganic acid halides, the product and yield depending on the reagent used: benzoyl halides give poorer yields than the corresponding aliphatic compounds [16,17]. Acetyl fluoride yields fluoroalkoxides, though SbF_3 is an alternative [18]. However, the most convenient reaction appears to be $Ti(OR)_4$ and TiX_4 (X = F,Cl,Br) mixed in the appropriate molar proportions.

All the halide alkoxides are hygroscopic and usually soluble in water without immediate decomposition, although on standing hydrated TiO_2 is the usual product.All are readily soluble in organic solvents.

Boiling $TiCl_4$ with phenol gives $Ti(OPh)_4$. At room temperature the number of chlorine atoms replaced depends upon the substituents of the phenol: for phenol and m-nitrophenol only one chlorine is replaced, for o- and p-nitrophenol, picric acid and β-naphthol two chlorines are replaced. A detailed study of $Ti(OPh)_2Cl_2$ [20] showed it to be a dimer in the solid state and in solution. Its main reactions are shown in figure 2.1. The expectation that this complex would lead to the synthesis of π bonded products with reducing agents has not been fulfilled.

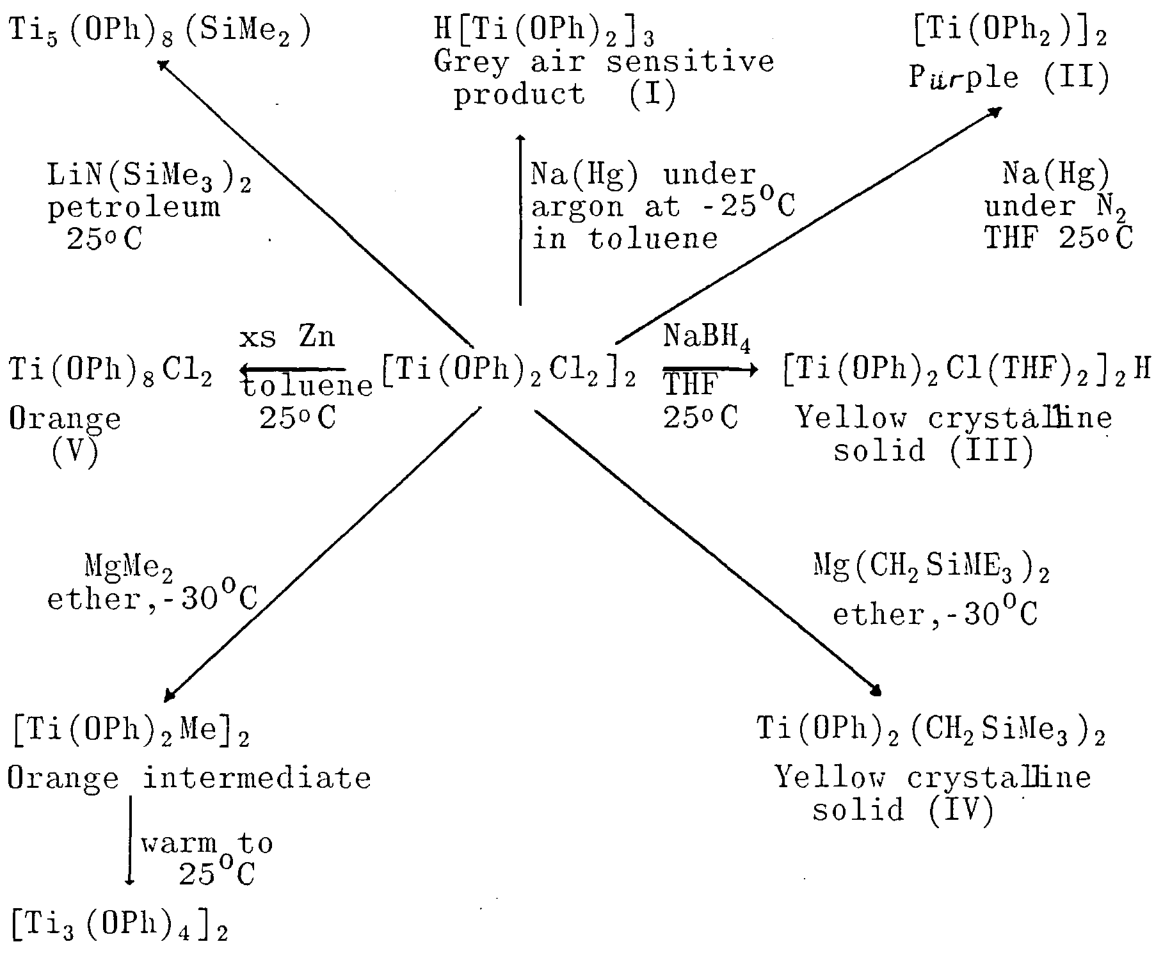
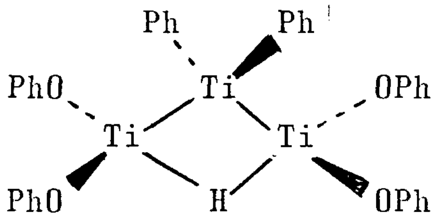


Fig 2.1 Some reactions of $[Ti(OPh)_2Cl_2]_2$



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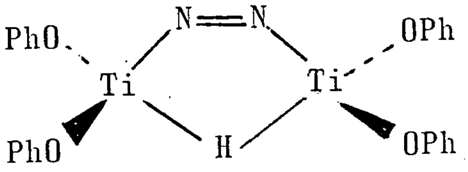

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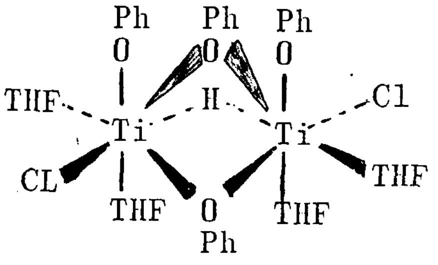

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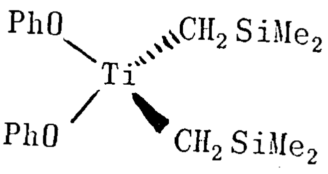

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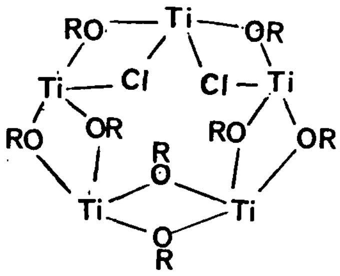


(V)

R= Ph

Compounds containing Ti-N,Ti-B and Ti-O-S linkages

Reactions of alkyl and aryl sulphonic acids with titanium alkoxides were investigated by Feld [19]. Mono- or disulphonates can be obtained, but substitution does not proceed further.

$$\mathrm{TiX_4} + n\mathrm{YOH} \longrightarrow (\mathrm{YO})_n\mathrm{TiX}_{(4-n)} + n\mathrm{HX}$$

Where $X = OPr^i$ or OBu^n, $Y = CH_3SO_2^-$ OR $PCH_3.C_6H_4SO_2^-$, $n=1$ or 2

Phosphinic acid yields di or trialkoxy titanium phosphinates, which are solids except for the viscous tributyl titanium benzenephosphinate.

$Ti(OBu)_4$ and benzene boronic acid yield $(BuO)_3TiOB(OH)C_6H_5$ two equivalents of $Ti(OBu)_4$ gives $[(BuO)_3TiO]_2BC_6H_5$ [12], both liquids. Reaction with boric acid yields alkoxy titanium borates [21]: R = butyl, aryl or 2ethylhexyl.

$$3\mathrm{Ti(OR)_4} + \mathrm{B(OH)_3} \longrightarrow \mathrm{[(RO)_3TiO]_3B} + 3\mathrm{ROH}$$

A series of N-methylaminoalkoxides of zirconium, $Zr(OPr^i)_{4-n}(OCHR'CH_2NR''R''')$ ($R' = R'' = H$, $R''' = Me$; $R' = H$, $R'' = R''' = Me$; $R' = R'' = R''' = Me$, $n = 1-4$) have been synthesized [22] by reaction of $Zr(OPri)_4.{}^iPrOH$ with aminoalcohols. These aminoalkoxides $Zr(OCHR'CH_2NR''R''')_4$ undergo insertion reactions with PhNCO to give products of the type $Zr(NPhCOOCHR'CH_2NR''R''')_4$ [23].

Organo-Alkoxy Derivatives

A large number titanium alkoxide derivatives containing cyclopentadiene ligands have been prepared and these have been comprehensively reviewed by Wilkinson [4].

Cyclopentadienyltitanium alkoxides can be prepared by the following methods:

$$2\mathrm{CpMgBr} + \mathrm{Ti(OBu)_4} \longrightarrow 2\mathrm{BuOMgBr} + \mathrm{(Cp)_2Ti(Bu)_2} \quad [24,25]$$

$$2\mathrm{CpNa} + \mathrm{TiCl_3(OEt)} \longrightarrow \mathrm{Cp_2TiCl(OEt)} + 2\mathrm{NaCl} \quad [25]$$

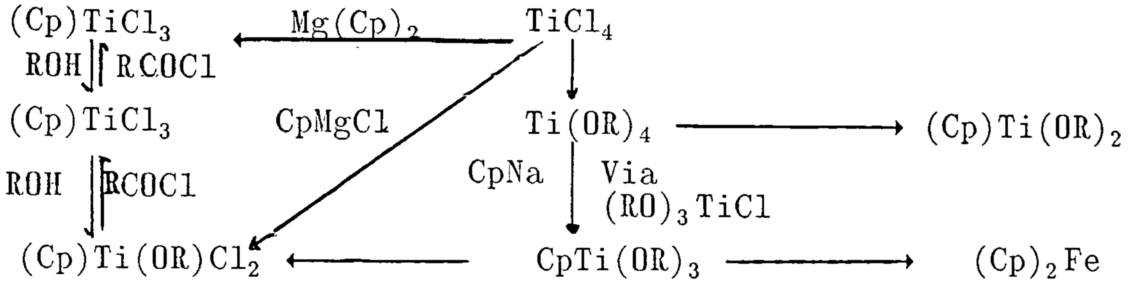
$$\mathrm{(Cp)_2TiCl_2} + \mathrm{EtOH} \xrightarrow[N_2]{\Delta} \mathrm{(Cp)Ti(OEt)Cl_2} \quad [26]$$

$$\mathrm{CpNa} + 2\mathrm{Ti(OEt)_2Cl_2} \longrightarrow \mathrm{CpTi(OEt)_3} \quad [27]$$

(Also for OPr^i and OBu^n derivatives.)

All $CpTi(OR)_3$ compounds are colourless liquids, sensitive to moisture, and monomeric in solution. $CpTi(OPr^i)_2Cl$ and $CpTi(OPr^i)Cl_2$ are yellow-green liquids.

Figure 2.2 gives some reactions of these complexes.



The reactions of alcohols with $CpTiCl_3$ are complex and only in a few cases give the trialkoxides:

$$TiCl_3Cp + 3ROH + 3NEt_3 \longrightarrow [Ti(OR)_3Cp] + 3Et_3N.HCl$$

Reaction with a number of phenols has also been successful. Exchange of OR groups in $Ti(OR)_3Cp$ is generally limited to certain phenols [28] and substituted cyclopentadienyl derivatives. The problems associated with the ready cleavage of the Ti-Cp bond may be overcome by using an ester instead of an alcohol [29]: $R = Pr^i$, hexyl or C_6H_4X.

$$[Ti(OEt)_3Cp] + 3\ ROAc \longrightarrow [Ti(OR)_3Cp] + MeCO_2Et$$

Mixed complexes such as $[TiCl_2(OCH_2CF_3)Cp]$ have to be prepared by indirect routes involving reaction of an azide complex $[TiCl_2(N_3)Cp]$ with the alcohol (CF_3CH_2OH) [30]. However, simpler routes have been developed, redistribution reactions being particularly convenient [28,29].

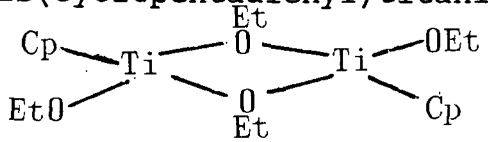
$$[Ti(OR)_3Cp] + 2[TiCl_3Cp] \longrightarrow 3[TiCl_2(OR)Cp]$$

$R = Et$, Ph or $p\text{NO}_2.C_6H_4$.

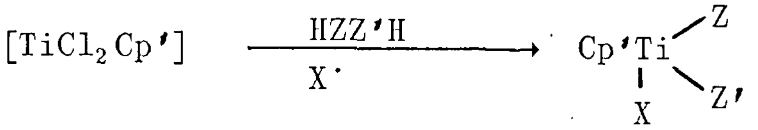
Careful control over stoichiometry generally gives the desired complex. Similarly the reaction of $[Ti(OR)_3Cp]$ with acyl halides can be controlled to give compounds of composition $[TiX_n(OR)_{3-n}Cp]$ (R = Et,Pr; X = F,Cl,Br,I; n = 1-

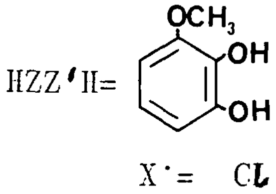
3) [27,31].

Reaction of the amide dimer $[\{Ti(NMe)_2Cp\}_2]$ with ethanol eliminates two molecules of amine to give a dimeric alkoxide, the first bis(cyclopentadienyl)titanium (III) alkoxide [32].



Low valent titanium compounds have been used as precursors for a number of Ti(IV) alkoxides. A route to chiral Ti(IV) alkoxides has been developed starting from Ti(III) compounds and a disymmetric phenol [33]:





In recent years many alkoxy and phenoxy derivatives containing ring-substituted cyclopentadienyl ligands have been prepared and the chiral nature of a number of these complexes has been carefully studied. For example, the reactions of various phenols (ROH) with $[TiCl_2Cp(\eta C_5H_4CHMe_2)]$ gave the corresponding $[TiCl(OR)Cp(\eta C_5H_4CHMe_2)]$, e.g. for R = 3-Me-6-$Pr^iC_6H_3$ and 2-{CH(Me)Ph}. In the latter case, two sets of diastereoisomers (separable by chromatography) were obtained, each set consisting of a racemic pair [34,35].

The mono Cp-Ti(IV) alkoxides and phenoxides are generally colourless or yellow solids or liquids. The alkoxides in particular have only moderate thermal stability. The hydrolytic stability depends markedly on the nature of the oxygen-bonded ligands. It has been found that substituents on the six-membered ring of a phenoxy substituent can exert a noticeable influence on the nature and stability of the Ti-Cp bond [28].

X-ray structural data for these compounds are relatively sparse. The pinacolate $[\{TiCl_2Cp\}_2O_2C_2Me_4]$ has a centrosymmetric structure in which two titanium units are bridged by a pinacolate dianion. Distances within the bridging ligand are similar to those in the free diol. The Ti-O bond length of 1.75Å is remarkably short, and together with a Ti-O-C angle of 166.2°, this was taken as evidence of Ti-O multiple bonding, i.e. the alkoxide behaving as a three electron ligand. Compounds of this general type are of interest as potential intermediates in transformations of the type

$$2R_2CO \xrightarrow{Ti} R_2C{=}CR_2$$

Mixed alkoxy complexes have been reported by Gervais and co-workers. For example:

$$[TiCl(OR_f)_2Cp] + LiMe \xrightarrow[ether]{-10^0C} [TiMe(OR_f)_2Cp] + LiCl$$

$$[Ti(OR)_3Cp] + MeMgI \longrightarrow [TiMe(OR)_2Cp] + MgI(OR)$$

Zirconocene alkoxides were first reported in the patent literature in 1960 [36] but the compounds were not fully characterised. The most common methods of preparation are:

(1) reaction of metallocene dihalide with the alcohol or phenol in the presence of an amine [37-41].

$$[MCl_2(\eta C_5H_5)_2] + 2ROH + 2NEt_3 \longrightarrow [M(OR)_2(\eta C_5H_5)_2] + 2NEt.HCl$$

(2) reaction of the tetracyclopentadienylmetal complex with an alcohol or phenol [37,42]

$$[M(C_5H_5)_4] + 2ROH \longrightarrow [M(OR)_2(\eta C_5H_5)_2] + 2C_5H_6$$

Other methods include reaction between $[\{ZrH_2(\eta C_5H_5)_2\}_n]$ and acetone to give $[Zr(OCHMe_2)_2(\eta C_5H_5)_2]$ [43], reaction of $[M(NMe_2)_2(\eta C_5H_5)_2]$ with an alcohol [44], or salt elimination between the metallocene dihalide and, for example, a sodium alkoxide [45].

The bis(cyclopentadienyl)metal alkoxides and phenoxides are typically white solids, readily soluble in organic solvents and can be crystallized from light petroleum. The phenoxides are generally stable to air in the solid state, but are more sensitive in solution [44].

Alkoxides and phenoxides of both zirconium and hafnium are cleaved by protic reagents. Hydrolysis of mono- and di-alkoxides of zirconium have been investigated: the mono-alkoxides gave the μ-oxo dimers, but similar reactions with di-alkoxides are more complex [39,46,47].

$$2[\mathrm{ZrCl(OR)}(n\mathrm{C_5H_5})_2] + \mathrm{H_2O} \longrightarrow [\{\mathrm{ZrCl}(\eta\mathrm{C_5H_5})_2\}_2\mathrm{O}] + 2\mathrm{ROH}$$

In contrast, atmospheric hydrolysis of $[\mathrm{ZrX(OEt)}(\eta\mathrm{C_5H_5})_2]$ during recrystallization has been reported to produce the μ-oxo complexes $[\{\mathrm{ZrX}(\eta\mathrm{C_5H_5})_2\}\{\mathrm{Zr(OEt)}(\eta\mathrm{C_5H_5})_2\}(\mu\mathrm{O})]$ [38].

Titanium alkoxides or alkoxy chlorides are highly active polymerization catalysts for ethylene, and are used in both reduced and supported systems [4]. Both titanium and zirconium alkoxides have been used to waterproof textile fabrics, especially leather, and also as paint drying agents and modifiers. The zirconium and hafnium alkoxides have been used in vapour deposition processes for depositing oxide films on graphite and for producing powders and fibres of ultra-high purity ceramic materials. Co-hydrolysis with silicon alkoxides shows promise in producing high purity specialized glass.

Vanadium, Niobium and Tantalum

The simple alkoxides of vanadium (IV) and (III) are well documented [48-52], as are the niobium and tantalum (IV) and (V) alkoxides [2,53-59], the latter compounds having detailed X-ray and NMR data available, giving an insight into bonding and structure.

Alkoxy Derivatives of Vanadium

Complexes of the type $V(OR)_nCl_{3-n}$ have been obtained from the reaction of VCl_3 with trialkylorthoformate under nitrogen [60]. The series $V(OR)Cl_2$ (R = Me, Et,Bu^n) are green solids which disproportionate under prolonged heating. Their general insolubility indicates a polymeric nature and IR studies indicate the presence of alkoxide bridges.

Winter and Kakos [48] have prepared a series of chloromethoxides of vanadium (III), e.g. $VCl_2(OMe).2MeOH$, by stepwise replacement of chlorine from VCl_3 in methanolic solution using an alkaki metal methoxide. Two molar equivalents of LiOMe gave a soluble form (A) and insoluble product (B). They are likely to represent two modifications of the solvated monochloride $VCl(OMe)_2.MeOH$. Form A readily loses the molecule of methanol on heating in vacuum, whilst crystalline form B decomposes. $VCl(OMe)_2$ from form A is soluble in acetone from which a monoacetate can be obtained. From the electronic spectra and magnetic measurements it was concluded that in $VCl(OMe)_2$ the vanadium atoms form trimeric clusters which associate through chlorine bridges to form an infinite lattice. Similar basic units were proposed for

$VCl(OMe)_2.MeCOMe$, but separated from each other by solvent molecules. For the soluble trimeric form A of $VCl(OMe)_2.MeOH$ a structure similar to that of $VCl(OMe)_2.MeCOMe$ was suggested, whilst for the insoluble tetrameric form B the vanadium atoms are situated at the corners of a rhombus. For $VCl_2(OMe).2MeOH$ a structure involving three octahedra sharing corners (OMe bridges) is suggested.

Reaction of R_4V (R = Me,Ph,CH_2Ph) and an alcohol ROH (R = Me,^{i}Pr,^{n}Bu,^{t}Bu) in ether or hexane solution at low temperatures gives complexes of the type $R_2V(OR)_2$ [61]. The stability of $(PhCH_2)_2V(OR)_2$ falls in the sequence ^{t}BuO > ^{i}PrO > ^{n}BuO > MeO. The methoxy complex is only seen at -30°C; the isopropoxy complex decomposes after 5 hrs. at 20°C. All are monomeric liquids, extremely sensitive to oxygen and moisture,which decompose on contact with aqueous solutions of mineral acids.

$[VOMe(OR)_2]$ (R = ^{i}Pr, ^{s}Bu, ^{t}Bu) may be prepared as brown liquids from $[VO(OR)_3]$ and $ZnMe_2$ in hexane at room temperature [62,63]. The reaction rate and thermal stability of the products depends upon the structure of the alkyl group R [64].

Phenyl vanadyl complexes $PhVO(OPr^i)_2$ and $PhVOCl(OPr^i)$ have been prepared by stirring $VO(OPr^i)_2Cl$ with PhLi and also $VO(OPr^i)Cl_2$ with Ph_2Hg in pentane at -50°C and -10°C respectively. Similar attempts to prepare $PhVO(OCH_2CF_3)_2$ have been reported unsuccessful.

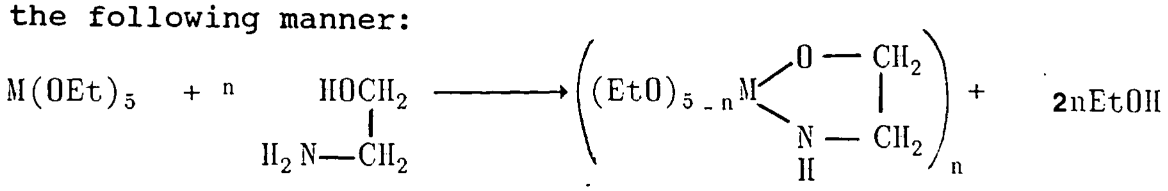
Gervais et al [65] have studied the reactions of fluoroalcohols R_fOH with vanadyl complexes. The inductive effect of the fluorine atoms in groups such as OCH_2CF_3, $OCH(CF_3)_2$ etc. was found to increase the sensitivity of the metal atom to nucleophilic attack. $VO(OR_f)_3$ and $VOCl(OR_f)_2$ were reported as the products of reaction of $VOCl_3$ and $CF_2HCF_2CH_2OH$, where $R_f = CF_2HCF_2CH_2$ [66], and also of $VOCl_3$ with $LiOR_f$ [65].

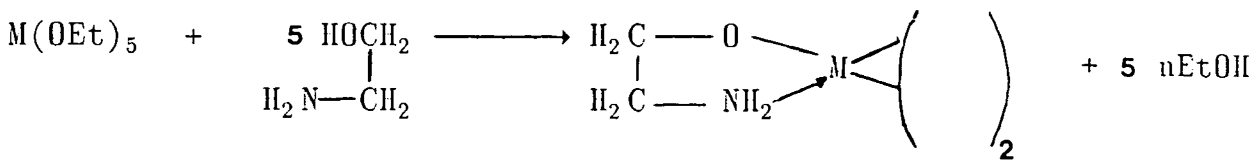
Alkoxy Derivatives of Niobium and Tantalum

NbX_5 and TaX_5 ($X = Cl,Br$) have been shown to react with oxygen donor ligands in anhydrous alcohol to yield halide alkoxide complexes of the type $M(OR)_3X_2L$ ($R = Me,Et$; $L = Ph_3PO, Ph_3AsO, Ph_2SO$ and $(Me_2N)_3PO$) [67]. Stepwise phenolysis in carbon tetrachloride yields $M(OPh)_nBr_{5-n}$ complexes. Crystalline, high melting point salts $[M(OPh)_4]SbCl_6$ have beensynthesized by reaction of $M(OPh)_4Cl$ with $SbCl_5$ in dichloromethane [68].Complexes of the type $M(OAr)_nCl_{5-n}$ were obtained from the reaction of phenol, naphthol and anthrol with MCl_5 in carbon disulphide solution [70].

A series of mixed alkoxy cyanides $M(OR)_{5-n}(CN)_n.xCH_3COOR$ ($R = Et, {}^iPr$; $n = 1-5$; $x = 0.5-2.5$) have been obtained from the metal pentalkoxide and pyruvonitrile in the required molar ratios [69].

$M(OEt)_5$ has been found to react with amino complexes in the following manner:



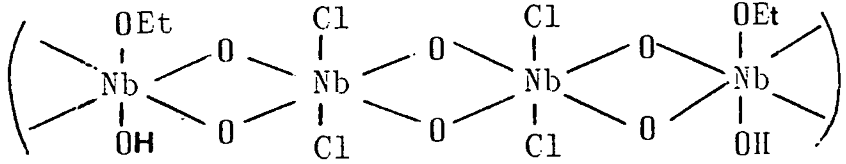


Riess [71] obtained products of the formula $NbCl_3(OR)_2HMPA$ (R = Me,^{i}Pr: HMPA = $OP(NMe_2)_3$) by the disproportionation of $[NbCl_2OR_2]$ in methylene chloride or ether in the presence of HMPA. X-ray crystallography on the isopropoxy derivative shows the two OR groups cis to each other and that the two $Nb-OPr^i$ bonds are of comparable lengths (1.81Å average), which implies a considerable $d_\pi-p_\pi$ contribution to the implicit bonding. A trans weakening was observed for the Nb-Cl bond trans to the OR group. The same geometrical isomer was always found to be the predominant species in the fresh solutions, whilst oxo species were detected in aged solutions.

Cotton [72] carried out a series of reactions with alcohols ROH (R = Me,Et,^{i}Pr) and $Nb_2Cl_6(THT)_3$ (1) (THT = tetrahydrothiophene) in toluene solution.With an excess of alcohol $Nb_2Cl_5(OR)(ROH)_4$ (2) ,R = Et,^{i}Pr, is the product, obtained as a yellow-brown or orange powder, or brown crystalline solid containing Nb(III) and being moderately stable at room temperature. Layering a solution of (2) in THF with hexane yields a red crystalline solid containing Nb(IV), the dimeric $Nb_2OCl_4(OR)_2(THF)_2$ (3). The one vacant coordination site is occupied by an oxygen atom from another dimer to give a tetramer. Complex (1) reacts with methanol at 5°C over several days to yield blue crystals, $Nb_2Cl_4(OMe)_4(MeOH)_2.2MeOH$ (4) a Nb(IV) species. A double Nb=Nb bond was assigned to complex (2) and a single one to (3) and (4). The bond in (2) is the shortest known double bond for a niobium or tantalum compound. The terminal alkoxy ligands form a very strong bond to the metal due to considerable π interactions, giving a nearly linear Nb-O-C bond angle. All the OH protons in (2) are involved in hydrogen bonding.

A number of niobium(V) oxyalkoxy derivatives $[NbO(OCH_2CF_3)_3.MeCN]_2$, $NbO(OCH_2CF_3)_2(OCH{=}CF_2)(CF_3CH_2OH)_{0.5}$, $[NbO(OEt)_3]_2$, $[NbOCl_2(OMe)CH_3OH]_2$ and $NbO(OCH_3)(OC_6H_4CHO)$ have been synthesized by direct alkoxylation of niobium oxychloride [69]. The molecular constitution of solutions of $[NbO(OEt)_3]_2$ and $[NbO(OCH_2CF_3)_3MeCN]_2$ in non-polar solvents was tentatively interpreted as a dynamic equilibrium between various μ-alkoxy and μ-oxo dimers, the latter being favoured by dilution. In polar media dimeric units are retained for $[NbO(OEt)_3]_2$, whilst the trifluoroethoxide derivative is split into monomeric species.

Polymeric complexes have been obtained by precipitation from 96% ethanol solutions with chloroform: $Nb_4O_6(OH)_2Cl_4(OEt)_2(bipy)_2$ and $Ta_6O_2(OH)_{18}Cl_6(OEt)_2(bipy)_2$. These complexes are colourless and amorphous solids, soluble in methanol, ethanol and water. They are not thermally stable, leading to linear polymers, the chains presumably terminating with bipy. The chemical and spectral evidence shows the complexes to comprise of coordinated bipy and OR groups linked by bridging M-O-M bonds [73].



Reynoud [75] obtained a series of alkoxy carbonyl derivatives of tantalum:

$$[Cp_2Ta(CO)(HOCH(Me)_2]^+PF_6^- + NaOH \longrightarrow CpTa(CO)(OCH(Me)_2)$$

$$[Cp_2Ta(CO)(HOMeEt)]^+PF_6^- + NaOH \longrightarrow Cp_2Ta(CO)(OCHMeEt)$$

$$[Cp_2Ta(CO)(HOPr)]^+PF_6^- + NaOH \longrightarrow Cp_2Ta(CO)(OPR)$$

All reactions yield green solids, and are carried out under an argon atmosphere, as both reactants and products are very air sensitive.

Complexes of the type $[MCl_{3-x}(OBu^t)_x(PMe_3)_2(C_2H_4)]$, x = 1 or 2, have been prepared and are used as metathesis catalysts for olefins [74]:

$$Ta(CH_2CMe_3)_2Cl_3 + Mg(OBu^t)Cl \xrightarrow{\text{ether}} \underset{\text{Yellow crystals}}{TaCl_2(OBu^t)(CH_2CMe_3)}$$

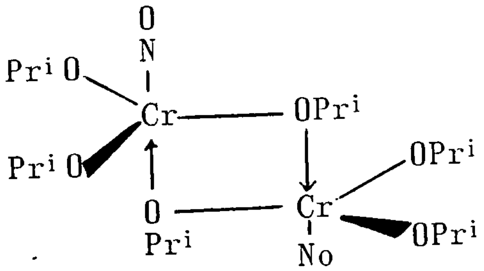
Chromium, Molybdenum and Tungsten

Of all the groups of transition metals this is the one which has the largest amount of published work relating to alkoxide chemistry, in particular the profusion of papers produced by Chisholm in the past three decades,which have lead to a greater understanding of the structural and bonding mechanisms in molybdenum and tungsten alkoxides. The simple alkoxides of molybdenum and tungsten are detailed in refs. [3,76-84], and those of chromium in refs. [85-94].

Alkoxy Derivatives of Chromium

Winter [95] has prepared a number of chloromethoxy derivatives of chromium (III) by reaction of the chloride with sodium methoxide in various solvents, yielding green, dimeric, hygroscopic complexes of the type $Cr(OMe)Cl_2.MeOH.L$, where L is solvent. Mehrotra has continued this study, extending it to include other alkoxides [96]. The replacement of OR groups with strongly electron withdrawing chlorine atoms as expected brings about significant changes in physical and structural characteristics of these derivatives,for example the enhanced Lewis acid behaviour of the chloroderivatives increases the tendency to form adducts with donor ligands.

A detailed study of the compounds $Cr_2(OPr^i)_6(NO)_2$, $Cr(OPr^i)_3(NO)L$ (L = NH_3,py or 2,4 lutidine) and $Cr(OBu^i)_3NO$ has been carried out [97]. These compounds have been prepared by reaction of monomeric $Cr(NPr^i_2)_3NO$ with alcohols in hydrocarbon solvents [98]. In both $Cr(OBu^i)_3(NO)$ and $Cr_2(OPr^i)_6(NO)_2$ the metal atom appears in either a local trigonal-bipyramidal or bipyramidal ligand field. The formal oxidation state of the metal is +2. The structure of $Cr_2(OPr^i)_6(NO)_2$ has been determined from physicochemical properties.



NMR studies below 0°C indicate the diastereotopic nature of the methyl groups of the terminal OPr^i ligands. The resonances coalese above 80°C to give a sharp doublet and septet indicative of rapid (NMR timescale) bridge terminal OPr^i ligand exchange.

Hydrocarbon solutions of chromocene react slowly with ^{t}butanol to give $CpCrOBu^t$, which is dinuclear with a nonplanar $(Cr\mu O)_2$ moiety. It is reactive towards a number of small unsaturated molecules, including acetylenes, CO, CO_2, nitric oxide and nitrous oxide [99].

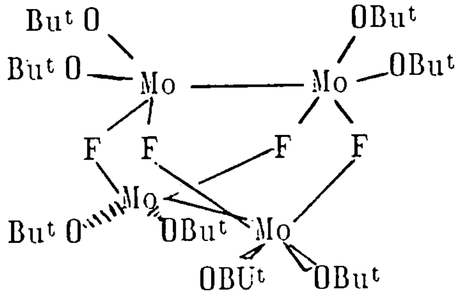
$Cr(CO)_6$ reacts with excess hydroxide ion in refluxing methanol to yield a polynuclear chromium tetranion $[Cr_4(CO)_{12}(\mu_3OMe)_4]^{4-}$, isolated as its R_4N^+ (R = Et,Me) salt. The anion consists of a distorted cubic Cr_4O_4 arrangement with triply bridging methoxy groups. With HCl in acetonitrile the complex reacts to yield $Cr(CO)_3(CH_3CN)_3$ [100]. $[Cr_4(CO)_{12}(\mu_3OR)_4]^{4-}$ (R = H,C_6H_5) have been prepared as their Et_4N^+ salts by reaction of $Cr(CO)_6$ with tetraethylammonium hydroxide in THF and tetraphenylammonium phenoxide in THF [101].

Alkoxy Derivatives of Molybdenum and Tungsten

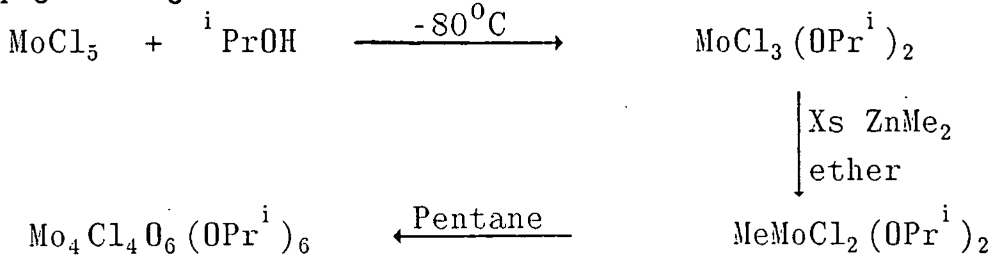
Molybdenum(III)

$Mo(OPr^i)_6$ reacts with chlorine, bromine and iodine in carbontetrachloride solution to yield tetrahalide products with the composition $Mo_2(OPr^i)_6X_4$, which are orange (X = Cl,Br) and brown (X = I) crystalline solids. Crystal structures of the chloro and bromo complexes show them to contain a central $Mo_2O_6X_4$ unit [102].

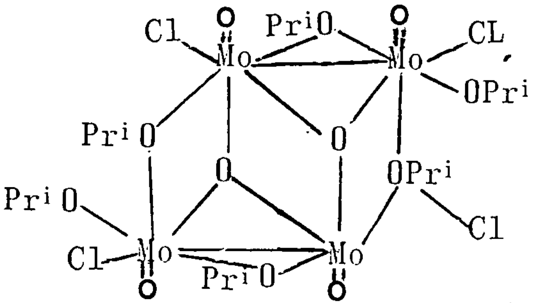
Reaction of $(^tBuO)_3Mo{=}Mo(OBu^t)_3$ in hydrocarbon solution with two equivalents of PF_3 yields a black, air-sensitive, hydrocarbon soluble solid of composition $MoF(OBu^t)_2$ [103]. The product is tetrameric, having the structure shown below.



Beaver and Drew [106] have obtained red crystals of $Mo_4Cl_4O_6(OPr^i)_6$ from the following reaction sequence:



The structure has been determined:



The Mo atoms are formally seven coordinate, with Mo-Mo distances of 2.669Å.

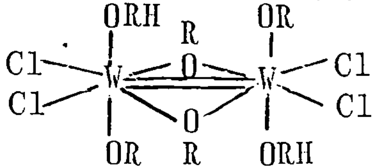
Molybdenum(IV)

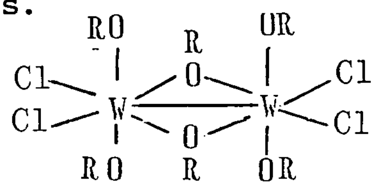
The reaction of $Mo_2(OBu^t)_6$ [104] and $Mo_2(OPr^i)_6$ [105] with molecular oxygen yields derivatives of the type $MoO_2(OR)_6$. With $Mo(OPr^i)_6$ an intermediate product $Mo_6O_{10}(OPr^i)_{12}$ was isolated and shown to contain a serpentine chain of molybdenum atoms with both six- and five-coordinated molybdenum atoms. The average oxidation state for molybdenum is 5.33 which leaves four electrons for metal-metal bonding, two localised single Mo-Mo bonds with length 2.585Å. Semi-bridging OR groups are seen here with a Mo····O distance of 2.88Å, too long for a regular bridging bond but much too short to be viewed as non-bonding.

Tungsten(IV)

The ditungsten alkoxide $W_2Cl_4(\mu OR)_2(OR)_2(ROH)_2$ (5)

possesses a W=W double bond characterized by a $\sigma^2\pi^2$ ground state electronic configuration and a strong hydrogen bond between syn-axial alcohol and alkoxide ligands [107]. The complex undergoes facile oxidation to a single bonded W(V) species $W_2Cl_4(\mu\text{-}OR)_2(OR)_4$ with oxygen, hydrogen peroxide, nitric oxide or silver (I) salts.





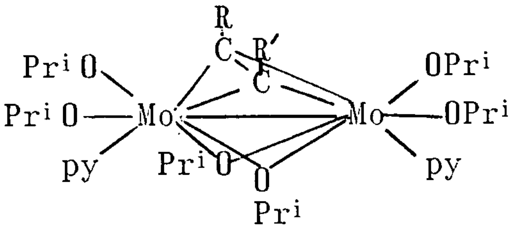
Compounds of type (5) bring about reductive coupling of ketones and yield products in which the organic molecules bridge the ditungsten centre.

The ethoxide complex (5) undergoes complete exchange with primary alcohols, but the more sterically demanding secondary alcohols give mixed alkoxides.

The complexes are remarkably thermally and air stable, whereas the molybdenum analogues are thermally unstable and very moisture sensitive. The increased stability of higher divalent tungsten alkoxides over the related molybdenum species correlates with the increased stability of the higher oxidation states as a transition metal group is descended.

Adduct Formation

In view of the known catalytic activity of molybdenum oxide compounds the reactions of molybdenum alkoxides with alkynes were studied [108]. $Mo_2(OPr^i)_6$ in hydrocarbon solutions reacts readily with alkynes RC_2R' ($R = R' = H$; $R = Me$, $R' = H$; $R = R' = Me$) at room temperature but the products could not be identified with certainty. In the presence of added pyridine however, crystalline solids of formula $Mo_2(OPr^i)_6(py)_2(RC_2R')$ were isolated from a hexane solution. The structure is shown below for the ethylene adduct.



The C-C distance of 1.368Å is longer than in ethylene and is among the longest known for $M_2(\mu C_2R_2)$ compounds. The Mo-C distances (2.09Å average) are shorter however.

The compound $Mo_2(OCH_2CMe_3)_6(HNMe_2)_2$ reacts similarly in hydrocarbon solvents with HC=CH to yield $Mo_2(OCH_2CMe_3)_6(HNMe_2)_2(C_2H_2)$.

A yellow crystalline nitrosyl complex $Mo(OR)_3NO$ has been obtained by reaction of $Mo_2(OR)_6$ (R = ^{i}Pr, ^{t}Bu and CH_2CMe_3) with nitric oxide [109]. These compounds are diamagnetic, dimeric and fluxional in solution. In $[Mo(OPr^i)_3NO]_2$ each Mo atom is five-coordinate in a trigonal bipyramidal manner and attains only a 14 electron configuration in the valence shell. The NO ligands occupy terminal axial positions and the two bridging OPr^i groups form short bonds in equatorial positions and long bonds in axial positions that are trans to NO ligands. The Mo···Mo separation is 3.335A, which precludes metal-to-metal bonding, the triple bond of the alkoxide thus being cleaved by addition of two nitrosyl ligands.

A similar tungsten derivative, $W(OBu^t)_3(NO)(C_5H_5N)$, has been isolated by the direct reaction between $W_2(OBu^t)_6$ and NO in pyridine solution [110]. The compound has a slightly distorted trigonal bipyramidal structure with the axial positions occupied by nitrosyl and pyridine ligands. The tungsten atom is displaced 0.34Å toward the nitrosyl ligand from the equatorial plane of the three alkoxy oxygen atoms.

Molybdenum Alkoxy Compounds with η^1 Carbon Ligands

Table 1 collects the syntheses of this type of complex.

TABLE 1 SYNTHESIS OF MOLYBDENUM ALKOXY COMPOUNDS CONTAINING η^1CARBON LIGANDS

	ALKOXY LIGANDS	COMPLEX	SYNTHESIS
1)	OR	$[(Mo_3(CO)_6(NO)_3(\mu OMe)_3(\mu_3 O))_2Na]^{3-}$	$Mo(CO)_6 + NaNO_2 + KOH, MeOH$
2)	μOR, $\mu_3 OR$	$[Mo_3(CO)_6(NO)_3(\mu OMe)_3(\mu_3 OMe)]^-$	$Mo(CO)_6 + NaNO_2 + KOH, MeOH$
3)	μOR OR	$[Mo_2(OBu^t)_4(\mu OBu^t)_2(\mu CO)]$	$[Mo(OBu^t)_6] + CO \xrightarrow[py\ rt]{}$
4)	OR	$[Mo(CO)_2(Py)_2(OBu^t)_2]$	$[Mo(OBu^t)_6] + CO$

The complex produced in reaction 1 contains the unusual triply bridging oxygen ligand. Table 2 gives structural information obtained from x-ray crystallography of these compounds.

TABLE 2 STRUCTURAL DETERMINATIONS OF MOLYBDENUM ALKOXY CARBONYL COMPOUNDS

COMPOUND	BOND DISTANCE (Å) AND ANGLE (°)	STRUCTURE
$Mo_2(OBu^t)_6(CO)$	Mo=Mo 2.498 $Mo-O_4$ 1.88 $Mo-O_6$ 2.08	Two bridging OBu^t, briding CO, two distorted square pyramids with CO apex.
$[Mo(CO)_2(py)_2(Bu^tO)_2]$	Mo-O 1.94 O-Mo-O 156	Distroted octrahedron
$[MeN]^+[Mo_3(CO)_6(NO)_3(\mu OMe)_3(\mu_3 OMe)]$	Mo-MO 3.428 (non bonding) μMo-O 2.11 μ_3Mo-O 2.22	Three OMe groups bridge edge of Mo_3 equilateral triangle, one OMe caps face.
$[PPN]_3^+[Na(Mo_3(CO)_6(NO)_3(\mu OMe)_3(\mu_3 O))_2]^{3-}$	Mo-Mo 3.297 (non bonding) μMo-OMe 2.19 μ_3O-OMe 2.05	Three OMe groups bridge edge of Mo_3 equilateral triangle, μ_3-O caps face.

The short Mo-O distance in the green, extremely air sensitive 16 electron complex $[Mo(CO)_2(py)_2(OBu^t)_2]$ (1.94Å) can be attributed to the substantial π donor ability of the butoxy ligand.This can also be seen in the low CO stretching frequencies observed in the IR spectrum.The metal electon density has been increased sufficiently to make the ν(CO) values of this formally Mo(II) complex comparable to most Mo(O) complexes.

Tungsten Alkoxy Complexes with η^1 Carbon Ligands

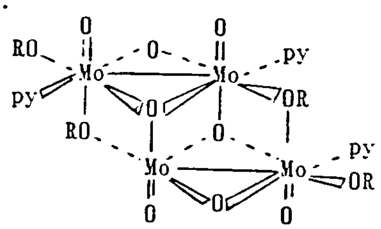
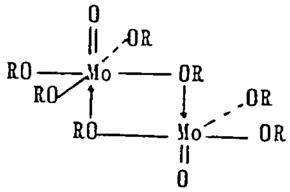
Many of the molybdenum compounds mentioned above have tungsten analogues and these will not be discussed here. A tungsten complex $[W_2(CO)_6(\mu\text{-}OEt)_3]^{3-}$ has been synthesized by reaction of a $[(arene)W(CO)_3]$ complex with $Et_4N^+OEt^-$ [114].

Since Mehrotra's major review of the transition metal alkoxy compounds in 1983 [3] an extensive study of molybdenum and tungsten alkoxide chemistry has been made by Chisholm and co-workers. Tables 3-6 present a review of the novel compounds synthesized in the last five years together with some important structural features.

TABLE 3 MOLYBDENUM ALKOXY COMPLEXES SYNTHESISED SINCE 1983

COMPOUND	SYNTHESIS		REF
$[Mo_6(\mu Cl)_8(OMe)_6]^{2-}$	$MoCl_2$ + NaOMe	$\xrightarrow{\text{MeOH}}$	[115]
$[Mo_6(\mu Cl)_8(OMe)_6]^{2-}$	$MoCl_2$ + NaOMe	$\xrightarrow{\text{MeOH}}$	
$Mo_2(OR)_2(SAr)_4$	$Mo_2(OR)_6$+mesitylene-thiol. R=Bu^t, CH_2Bu^t	$\xrightarrow[\text{carbon}]{\text{hydro-}}$	[116]
$MoO_2(OR)_6$	$Mo_2(OR)_6 + O_2$	$\xrightarrow[\text{carbon}]{\text{hydro-}}$	[117]
$MoO(OR)_4$	$[Mo(OR)_4]_x + O_2$ R=Bu^t, x=1, R=Pr^i, x=2 R=CH_2Bu, x ⩾ 2	$\xrightarrow[\text{carbon}]{\text{hydro-}}$	
$Mo_2(OCH_2Bu^t)_4(HNMe_2)_4$	$Mo_2Bu^i_2(NMe_2)_4$+ROH R= Bu^tCH_2	$\xrightarrow{\text{hexane}}$	[118]
$Mo_2Bu^t(OBu^t)_5$	$Mo_2Bu^i_2(NMe_2)_4$+ROH R= Bu^t	$\xrightarrow{\text{hexane}}$	
$Mo_2(OPr^i)_4(HNMe_2)_4$	$Mo_2Bu^i_2(NMe_2)_4$+ROH R= Pr^i	$\xrightarrow{\text{hexane}}$	
$Mo_2(OCH_2Bu^t)_4(MeCOCHCOMe)_2$-$(Bu^tNO)_2$	$Mo_2(OCH_2Bu^t)_4(MeCOCHCOMe)_2$+ Bu^tNC	$\xrightarrow{\text{hydrocarbon}}$	[119]
[W]$Mo(OBu^t)_4(NNCPh_2)$	$Mo_2(OBu^t)_6$ + Ph_2CNN	$\xrightarrow[\text{carbon}]{\text{hydro-}}$	[120]
[W]$Mo_2(OPr^i)_4[N(C_6H_5)C(O)$-$OPr^i]_2$	$Mo_2(OPr^i)_6$ + Phenyl-isocynates	$\xrightarrow[\text{solvent}]{\text{non polar}}$	[121]
[W]$Mo_2R_2(OR')_4$	$Mo_2R_2(NMe_2)_4$ + R'OH R=Me, R'=Bu^t; R=CH_2Ph, $pCH_2C_6H_4Me$, R'= Pr^i; R=CH_2CMe_3, R'=Pr^i, Et, CH_2CMe_3	$\xrightarrow[\text{carbon}]{\text{hydro-}}$	[122]
$Mo_2(OCH_2Bu^t)_6(\mu R_2NCN)$	$Mo_2(OCH_2Bu^t)_6$(M=M) +R_2NCN, R=Me, Et	$\xrightarrow[\text{carbon}]{\text{hydro-}}$	[123]
$Mo_4(\mu_3N)_2(\mu OPr^i)_2(OPr^i)_{10}$	$2(Bu^t)_3Mo{=}N$ + $Mo_2(OPr^i)_6$.	$\xrightarrow[\text{PrOH}]{\text{hexane}}$ 25°C	[124]
$Mo_2(OPr^i)_4(dmpe)_2$	$Mo_2(OPr^i)_4(HOPr^i)_4$ +2dmpe	$\xrightarrow[\text{22°C}]{\text{hexane}}$	[125]
[W]$Mo_2(OR)_6X_4$	$Mo_2(OR)_6$ +CCl_4, CH_2Br	$\longrightarrow$	[126]
$Mo_4F_4(OBu^t)_8$	$Mo_2(OBu^t)_6$ +$2PF_3$	$\xrightarrow[\text{carbon}]{\text{hydro-}}$	[127]
$Mo[HB\{C_3HMe_2N_2\}_3](NO)I(OEt)$	$Mo[HB\{C_3HMe_2N_2\}_3](NO)I_2$ +EtOH	$\xrightarrow{\text{reflux}}$	[128, 129]

TABLE 4 STRUCTURAL FEATURES OF MOLYBDENUM ALKOXY COMPLEXES

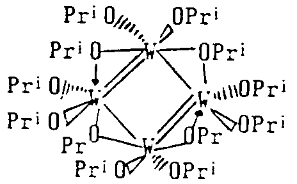
COMPOUND	Structural Features	REF
$[Mo_6(\mu_3Cl)_8(OMe)_6]^{2-}$ $[Mo_6(\mu Cl)_8(OMe)_6]^{2-}$	Subsitution of terminal Cl for OMe causes little change in M-M distance, but replacing μ_3Cl by μ_3OMe causes substantial shorting.	[115]
$Mo_2(OR)_2(SAr)_4$	Less air sensitive than alkoxide. Anti or rapidly interconverting anti and gauche rotamers of ethane-like dimers $(RO)(ArS)_2Mo{\equiv}Mo(SAr)_2(OR)$, Mo-Mo 2.230Å	[116]
$MoO_2(OR)_6$ $MoO(OR)_4$	R=Pr^i, CH$_2$Bu^t intermediate $Mo_3O(OR)_{10}$ and $Mo_6O_{10}(OPr^i)_{12}$ isolated and characterised. $MoO_2(OR)_2(bipy)$ (R=Pr^i, CH$_2$Bu^t). $Mo(\mu_3O)(\mu_3OR)(\mu OR)_3(OR)_6$ (R=Pr^i, CH$_2$Bu^t), $Mo_4O_{10}(OPr^i)_{12}$ characterised $MO_4O_8(OPr^i)_4(py)_4$  $MoO(OR)_4$  Products all yellow liquids or colourless solids, moisture and air sensitive.	[117]
$Mo_2(OCH_2Bu^t)_4(HNMe_2)_4$ $Mo_2Bu^t(OBu^t)_5$ $Mo_2(OPr^i)_4(HNMe_2)_4$	$Mo_2(OCH_2Bu^t)_4(HNMe_2)_2$ contains a M≣M quadruple bond R=Pr^i complex reactive towards ethylene ($Mo_2(C_2H_4)$-$(OPr^i)_5$ (M≡M) and neutral donor ligands $Mo_2(OPr^i)_4L_4$ (M≣M) L=py, H$_2$NMe, PMe.	[118]
$Mo_2(OCH_2Bu^t)_4(MeCOCHCOMe)_2$ $(Bu^tNO)_2$	First reaction where an Mo-Mo multiple bond is not cleaved by isocyanide ligands. The unbridged Mo≡Mo bond ($\sigma^2\pi^4$) is converted to an edge bridged d^3-d^3 dimer of formal configuration $\sigma^2\pi^2\delta^2$, and is accompanied by an increase in the Mo-Mo distance from 2.237 to 2.508Å. The alkoxide-β diketone derivatives are markedly less reactive towards π acid ligands than the alkoxides.	[119]
[W]$Mo(Bu^tO)_4(NNCPh_2)$	The dinuclear centre serves as a source of electrons for the reduction of the diazoalkane to a 2-e ligand. The crystalline NNCPh$_2$ complex has a trigonal bipyramidal central MoO_4N moiety Mo-O = 1.944Å Mo-Oeq= 1.889A. Adducts are formed with pyridine .$W_2(OBu^t)_6$-$(\mu NNCAr_2)_2$. Ar=Ph, p-tolyl. The molecular structure of the p-tolyl derivative contains a central $[O_3W$-μ-$N]$ moiety based on the fusing of two trigonal bipyramidal units sharing a common equatorial- axial edge formed by a pair of $NNCAr_2^{2-}$ ligands. W-W distance = 2.675Å (single bond)	[120

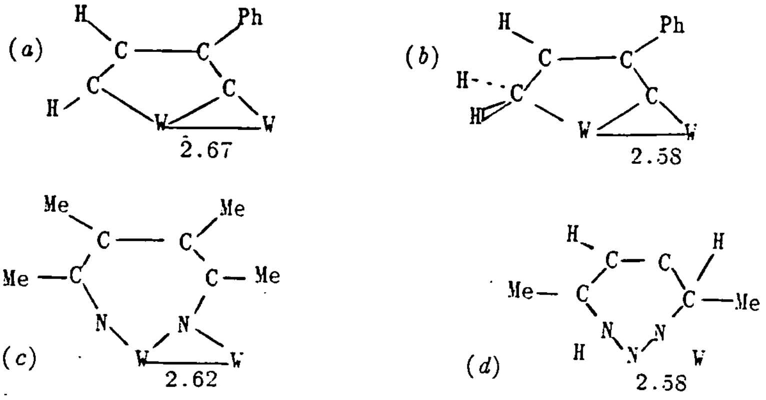
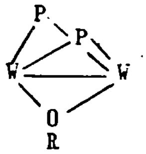
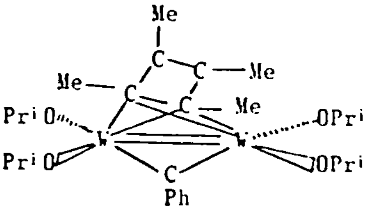
Compound	Structural Features	REF
[W]$Mo_2(OPr^i)_4[N(C_6H_5)C(O)$ $-OPr^i]_2$	Reaction involves insertion into Mo-OR bond.Two cis bridging bidentate ligands, each Mois in the +3 oxidation state and Mo-Mo=2.221Å (triple bond) [W≡W= 2.290Å]	[121]
[W]$Mo_2R_2(OR')_4$	Depending on the steric properties of R and R' these compounds may be coordinatively unsaturated and can be isolated as Lewis base adducts . These steric properties are crucial as assuming that protolysis of the Mo-C(alkyl) bond does not occur rapidly,eg OPr^i gives $Mo_2R_2(NMe_2)_2(OR')_2$,detectable for bulky R,R'. Reactions with β-H containing ligands give $Mo_2R(OR')_5$.	[122]
$Mo_2(OCH_2Bu^t)_6(\mu R_2NCN)$	Cyanamide bridges the two Mo atoms parallel to the Mo-Mo bond, length 2.449Å Mo-O(terminal) 1.91Å, indicating some πdonation from OR to Mo.Trans influence R_2NCN lengthens trans Mo-O bond to1.954 Å.	[123]
$Mo_4(\mu_3N)_2(\mu OPr^i)_2(OPr^i)_{10}$	Centrosymmetric molecules.Coordination about N is T shaped,while about each Mo it corresponds to a trigonal bipyramid.Two long(2.92Å) and two short (2.55Å) Mo-Mo bonds.	[124]
$Mo_2(OPr^i)_4(dmpe)_2$	$Mo_2(OR)_4L_4$ ($R=Pr^i$, $L=Pr^iOH$,py,R=Np,$L=HNMe_2$,PMe_3) contains d^4Mo(II)-d^4(II)centre with an eclipsed $Mo_2O_4L_4$ skeleton.πdonor alkoxides lengthen and labilize the Mo-Mo quadruple bond .DMPE complex air sensitive crystalline compound.DMPE acts as a chelating agent to one Mo atom, the OR ligands are bonded to the second Mo atom. The $Mo_2O_4P_4$ unit adopts a staggered conformation. This is the only example of an unsupported M-M multiple bond uniting Mo(0) and Mo(IV), the bonding being triple,$\sigma^2\pi^4$.	[125]
[W]$Mo_2(OR)_6X_4$	W more reactive than Mo ,C-Br>C-Cl.Several products including $M_2X_4(OR)_6$ compounds $Mo_2(OCH_2Bu^t)_6Br(py)$(M=M) has a highly distorted confacial bioctahedral molecular structure with one bridging bromine atom, two briding OR ligands Mo-Mo distance =2.534Å	[126]
$Mo_4F_4(OBu^t)_8$	Complex contains a bispheroid of Mo atoms with two short Mo-Mo bonds (2.26A) and four (3.75A) long corresponding to localised Mo-Mo and non -bonding distances respectively.Can be viewed as a dimer. [$Mo_2F_2(OBu^t)_4$ PPh_3 adducts can be formed having an unbridged Mo-Mo bond 2.27Å. This is the first compound containing F ligands attached to$(Mo\equiv Mo)^{6+}$ The choice of bridging ligands is F over OBu^t which may be due to the greater π donor properties of OBu^t.By remaining terminal and cis the π donation to the metal can be maximized.	[127]
$Mo[HB\{C_3HMe_2N_2\}_3](NO)$ $I(OEt)$	Air stable,green crystalline solid .Similar reactions occur with PhOH and its derivatives.	[128 129]

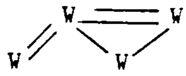
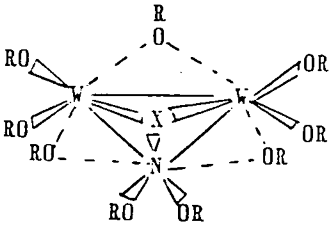
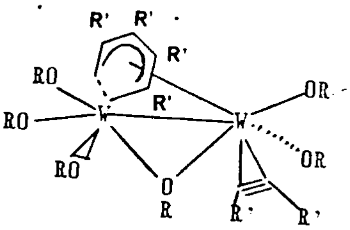
TABLE 5.TUNGSTEN ALKOXY COMPLEXES SYNTHESISED SINCE 1983

COMPOUND	SYNTHESIS		REF
$W_2(OPr^i)_6$	$W_2(OBu^t)_4 + {}^iPrOH$	$\xrightarrow{(MeOCH_2)_2}$	[130-132]
$(W_4(OPr^i))_{12}$	$W_2(OBu^t)_4 + {}^iPrOH$	$\xrightarrow{(MeOCH_2)_2}$	
$W_4(H)_2(OPr^i)_{14}$	$W_2(NMe_2)_6 + {}^iPrOH$	$\xrightarrow{Hexane.\ rt}$	[133]
$W_4(C)(NMe)(OPr^i)_2$	$W_2(NMe_2)_6 + {}^iPrOH$	$\xrightarrow{Hexane.\ rt}$	
$W_2(OCH_2Bu^t)_6(NCNMe_2)_3$	$W_2(OCH_2Bu^t)_6(HNMe_2)(M{=}M)$ $+ Me_2NCN$	$\xrightarrow{0°C}$	[134]
$W_3(\mu NH)(OPr^i)_{10}$	$W_2(OPr^i)_6(py)_2$ $+(Bu^tO)_3W\equiv N$	$\xrightarrow[22^0C]{Hexane.PrOH^i}$	[135]
$W_2(OBu^t)_6(CHCHC(Ph)N)$ *a*	Alkyne adduct of $W_2(OR)_6$ +		
$W_2(OPr^i)_7(CHCHC(Ph)N)$ *b*	nitrile	$\xrightarrow{hydrocarbon}$	[136]
$W_2(OCH_2Bu^t)_6(N(CMe)_4N(Py)$ *c*	$W_2(OBu^t)_6(\mu\ H_2)(py)$ + $PHC\equiv N$		
$W_2(OPr)_7(NHC(Me)CHCH(Me)N)$ *d*			
$W_2(OBu^t)_6(\mu CO)$	$W_2(OBu^t)_6 + CO$	$\xrightarrow{Hexane}$	[137]
$[W_2(OPr^i)_4(\mu CO)]_2$	$W_2(OBu^t)_6 + {}^iPrOH$	$\xrightarrow{Hexane}$	
$W_2(OPr^i)_6(py)(\mu P_2)$	$W_2(OPr^i)_6(py)_2$ $+ Co_2(\mu P_2)(CO)_6$	$\xrightarrow{Hexane}$	[138]
$W_2(OPr)_6(\mu C_4Me_4)(\eta^2C_2Me_4)$	$W_2(OPr^i)_6(py)_2$ $+ MeC\equiv CMe$	$\xrightarrow{Hexane}$	[139]
$W_3(\mu_3CMe)(\mu OPr^i)_3(OPr)_6$	$W_2(OPr^i_t)_6(py)_2$ $+ (BuO^t{}_3)W\ CMe$	$\xrightarrow[HOPr^i]{Hexane}$	[140]
$W_3(H)(OPr)_4(\mu C_4Me_4)(\mu CPh)$	$W_2(CH_2Ph)_2(OPr^i)_4(W\equiv W)$ $+MeC\equiv CMe$	$\xrightarrow{Hexane}$	[141]
$W_4(p\text{tolyl})_2(OPr^i)$	$W_2(p\text{tolyl})_2(NMe_2)_4$ $+5\ PrOH$	$\xrightarrow[0^0C]{Hexane}$	[142]
$[(HNMe_2)(EtC\equiv)({}^iPrO)_2W\text{-}(\mu\ OPr^i)]$ (1)	$W_2(OPr^i)_6(HNMe_2)_2$ $+3\ Hexyne$	$\xrightarrow[RT]{Pentane}$	[143]
$W_3(\mu_3CEt)(OPr^i)_9$ (2)	$W_2(OPr^i)_6(HNMe_2)_2$ $+3\ Hexyne$	$\xrightarrow[RT]{Pentane}$	
$W_2(\mu C_4Et_4)(\eta^2C_2Et_2)(OPr)_6$ (3)	$W_2(OPr^i)_6(HNMe_2)_2$ $+3\ Hexyne$	$\xrightarrow[RT]{Pentane}$	
$W_2(\mu CSiMe)_2(OBu^t)_2(CH_2SiMe_3)$	$W_2(\mu CSiMe)_2(CH_2SiMe_3)_4$ $+Bu^tOH$	$\longrightarrow$	[144]
$W\{HB(Me_2pz)_3\}(NO)Cl(OPh)$	$W\{HB(Me_2pz)_3\}(NO)Cl_2$ $+PhOH$	$\xrightarrow[reflux]{CH_2Cl_2}$	[145]

TABLE 6. STRUCTURAL FEATURES OF TUNGSTEN ALKOXY COMPOUNDS

COMPOUND	STRUCTURAL FEATURES	REF
$W_2(OPr^i)_6$ $W_4(OPr^i)_{12}$	Short W-W bonds in $W_2(OPr^i)$ imply strong O→W πback bonding.[$W_4(OPr^i)_{12}$] contains two short (double) and two long W-W bonds (2.502, 2.733 Å).  The central W_4 moiety is planar: the W_4 unit can be discrib ed as a distorted rhombus or a flattened butterfly.	[130-132]
$W_4(H)_2(OPr^i)_{14}$ $W_4(C)(NMe)(OPr^i)_2$	$W_2(OPr^i)_6(HNe_2)_2$ is the major product at short reaction times. The carbide complex is a persistent impurity. Th structure is based on a $W_4(C)(N)O_{12}$ skeleton. Th W_4 centre is formally 18+ having only 6 electrons for M-M clusters bonding. W-W distance =2.78Å (av), notably longer than the 12e- cluster M_4 butterflies.	[133]
$W_2(OCH_2Bu^t)_6(NCNMe_2)_3$	Xray study reveals loss of the triple bond: W-W=3.85Å, nonbonding and formalreduction of each M_2NCN molecule to a 2-ligand for which three modes of bonding are seen.	[134]
$W_3(\mu NH)(OPr^i)_{10}$	The imido capped cluster is isomorphous with $W_3(\mu_3O)(OPr^i)_{10}$. It adopts an M_3X_{11} skeletal geometry. The dimensions are up to 30σ larger than those for the oxo-capped compound W - W 2.556Å.	[135]
$W_2(OBu^t)_6(CHCHC(Ph)N)$ *a* $W_2(OPr^i)_7(CHCHC(Ph)N)$ *b* $W_2(OCH_2Bu^t)_6(N(CMe)_4N(Py)$ *c* $W_2(OPr)_7(NHC(Me)CHCH(Me)N)$ *d*	Each W atom is in a trigonal bipyramidal environment with the metal atoms joined along a common equatorial -axial edge through an alkoxide ligand and an N of the metallocyclic ring formed by coupling of the alkyne and the nitrile. Formally this can be counted as a 4- ligand with terminal allylidene and imido groups W=CHCH=C(Ph)N=W. W-W distance = 2.674Å (single bond). $W_2(OPr^i)_2(CH_2CHC(Ph)N)$ *b* is formed by the reaction of (*a*) with Pr^iOH. Each W atom is octahedrally coordinated and the two metal atoms share a face formed by the two bridging OR ligands and the N atom of the metallacycle that is now formally a 3- ligand having imide and alkyl attachments to W_2, W-W distance= 2.585Å. $W_2(OCH_2Bu^t)_6(N(CMe)_4N)(py)$ (*c*) has a 7 membered metallacycle that incorporates the 4- ligand derived from 1.4 -diamino 1,2,3,4tetramethyl 1.3 butadiene. Connectivity involes one terminal and one bridging imido group. W-W distance =2.617Å. $W_2(OPr^i)_7(NHC(Me)CHCH(CMe)N)$ (*d*) is closely related to (*c*) and the conversion parallels that of (*a*) to (*d*).	[136]

	The 7 membered metallacycle has a terminal amido group (1-) and a bridging amido group (2-) W - W distance=2.576Å  	
$W_2(OBu^t)_6(\mu CO)$ $[W_2(OPr^i)_4(\mu CO)]_2$	Complex isomorphous with Mo analogue.Contains central $W_2(OBu^t)_2(\mu CO)$ unit W-W distance =2.526Å. Each W atom is in a square based pyramidal geometry with μCO occupying the apical position. $[W_2(OPr^i)_6(\mu CO)]_2$ contains an essentially planar central $[W_2(\mu CO)]_2$ unit with W-W distance=2.657Å .Each W atom is in a trigonal bipyramidal enviroment. The reaction sequence is of stepwise reduction in W-W and C-O bond order from 3→2→1	[137]
$W_2(OPr^i)_6(py)(\mu P_2)$	Central pseudo tetrahedral W_2P_2 moiety with essentially single bond W-W distances.This is an analogue of the $W_2(OR)_6(py)(\mu C_2H_2)$ complexes. 	[138]
$W_2(OPr)_6(\mu C_4Me_4)(\eta^2 C_2Me_4)$ $W_3(\mu_3 CMe)(\mu OPr^i)_3(OPr)_6$	The crystal structure of the W complex shows each W coordinated to five ligands so that the local geometry about each W is a square based pyramid. Three units are fused together through $\mu_3 CMe$ ligands and three basal μOR ligands W-W distance=2.75Å.	[139-140]
$W_3(H)(OPr)_4(\mu C_4Me_4)(\mu CPh)$	Initial product is $(\eta^2 c_2Me_2)(PhCH_2)(\mu OR)_2W(OPr^i)(CH_2Ph)(\eta^2 C_2Me_2)$ which has a puckered central $W_2(\mu OR)_2$ core, W-W distance = 2.67Å 	[141]

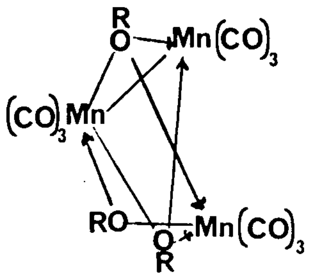
$W_4(p\text{tolyl})_2(OPr^i)$	The nmr is consistent with a static cluster having two unequivalent aryl groups and ten unequivalent OPr^i ligands, each having diastereotopic methyl groups. The 12e- W_4 cluster is a grossly distorted rhombus of metal atoms.  	[142]
$[(HNMe_2)(EtC\mu_3)(^iPrO)_2W(\mu\ OPr^i)]$ (6) $W_3(\mu_3CEt)(OPr^i)_9$ (7) $W_2(\mu C_4Et_4)(\eta^2C_2Et_2)(OPr)_6$ (8)	(6) adopts an edge-shared bioctrahedral geometry in the solid state. (7)  $R=Pr^i, X=CEt$ (8)  $R=Pr^i, R'=Et$	[143]
$W_2(\mu CSiMe)_2(OBu^t)_2(CH_2SiMe_3)$	The product is obtained as a mixture of two isomers, the minor isomer being isolated by fractional crystallisation.	[144]

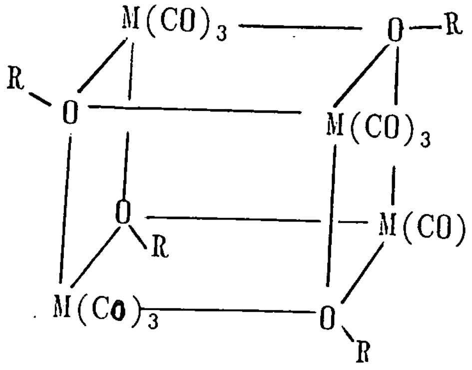
Manganese, Technetium and Rhenium

The simple alkoxides of manganese have been little studied [86,146] and there are no known analogues for technetium and rhenium except a hexamethoxide of the latter [76].

Alkoxy Derivatives of Manganese

Abel et al [147] have studied the reactions of $Mn(CO)_5Br$ with ethanol, ^{i}propanol and ^{n}butanol, and triethylamine. An ethoxide derivative $[Mn(CO)_3(OEt)]_3$ was obtained as red crystals but low and erratic yields were reported with the other alcohols. However, $[Mn(CO)_3(OR)]_3$ complexes were obtained successfully for R = Me,Et,^{i}Pr,^{n}Bu,C_6H_{11}, $CH_2CH=CH_2$,CH_2Ph using $Me_3Sn(OR)$. All the products were trimeric, with the exception of the reaction with benzyl alcohol where a tetramer was the major product. The IR and ${}^1H$ and ${}^{13}C$ NMR spectra suggested a symmetrical cubic structure for the tetramer as opposed to the remarkably unsymmetric structure based on a scalene triangle of metal atoms proposed for the trimer [147,148].





Phenyldimethylphosphine reacts with $[Mn(CO)_3(OEt)]_3$ to displace one carbonyl group yielding $Mn_3(CO)_8(PMe_2Ph)(OEt)_3$ which shows two different environments for the ethoxide groups. The structure is that of the parent complex.

Interaction of $Mn_3(CO)_9(OEt)_3$ with phenol [147] brings about replacement of only one ethoxide group. Of the three ethoxide groups, the formally five electron donor face-bridging groups will have no nucleophilic character, but the edge-bridging oxygen atom still formally has one lone pair of electrons available for reaction. Thus PhO replaces the edge-bridging ethoxide group and this has been confirmed by ^1H NMR.

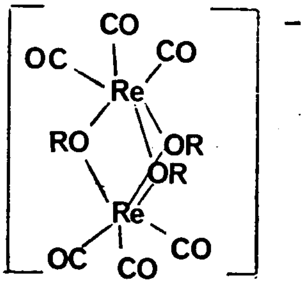
Reactions of $Mn_3(CO)_9(\mu_3OEt)_2(\mu_2OEt)$ have been studied with BX_3 (X = F,Cl,Br,I) [149] and the halide complexes $Mn_3(CO)_9(\mu_3OEt)_2(\mu_2X)$ have been isolated; the Cl and Br products have also been prepared from the reactions of anhydrous HX.

Reaction of $[Mn\{N(SiMe)_3\}_2(THF)]$ and $LiN(SiMe_3)_2$ in hexane with $^tBu_3COH$ in THF yields pale pink, highly air and moisture sensitive crystals of $[Li\{Mn(N(SiMe_3)_2)(OCBu^t{}_3)_2\}]$ [150]. The geometry of the manganese atom is distorted trigonal planar. The complex is unique in being an example of a three coordinate complex of manganese(II). The Mn-O distance is comparatively short and the steric congestion is seen from the fact that it doesnot form a tris(alkoxy) complex even when heated with excess $^tBu_3COH$ in refluxing toluene. Reaction of the parent compound with less sterically demanding alcohols such as $^tBu_2CHOH$ in refluxing benzene or hexane yields the trimeric $[Mn_3(OCH^tBu_2)_6]$, which contains two three-coordinate manganese atoms and a central four-coordinate metal atom [151]. It is the first homoleptic manganese(II) alkoxide to be structurally characterized. The complex is non-linear, with a Mn-Mn-Mn bond angle of 154° and no formal Mn-Mn bonds. The central Mn-O distance is the longest, the terminal Mn-O the shortest.

Alkoxy Derivatives of Rhenium

With the exception of the triply alkoxy-bridged carbonyl anions $[(CO)_3Re(\mu OR)_3Re(CO)_3]^-$ (R = Et,Pr^i) [152] other alkoxy species of rhenium have only one alkoxy group and contain tertiary phosphine, methyl and acetate groups, or nitrosyl ligands.

Reaction of ReH_9^- and carbon monoxide in alkaline alcoholic media yields a binuclear carbonyl hydride anion and also a carbonyl alkoxide anion, with the three bridging OR groups mentioned above, formulated as:



$R = Pr^i, Et$

[152]

Reaction of $(Et_3N)_2ReH_9$ with CO in refluxing solution with 2-propanol formed a red precipitate shown to be a mixture of hydrides. This precipitate was collected and the yellow filtrate obtained gave an off-white precipitate of $Et_4N[Re_2(CO)_6(OPr^i)_3]$ on addition of water. This complex then gives the following reactions:

$$\begin{tikzcd}
{[Re_2(\mu OPr^i)_3(CO)_6]^-} \arrow[rr, "HX\ 25^oC"'] \arrow[d, "HX"] & & {[Re_2X_3(CO)_6]^{2-}} \\
{[ReX_3(CO)_3]^{2-}} & &
\end{tikzcd}$$

[153]

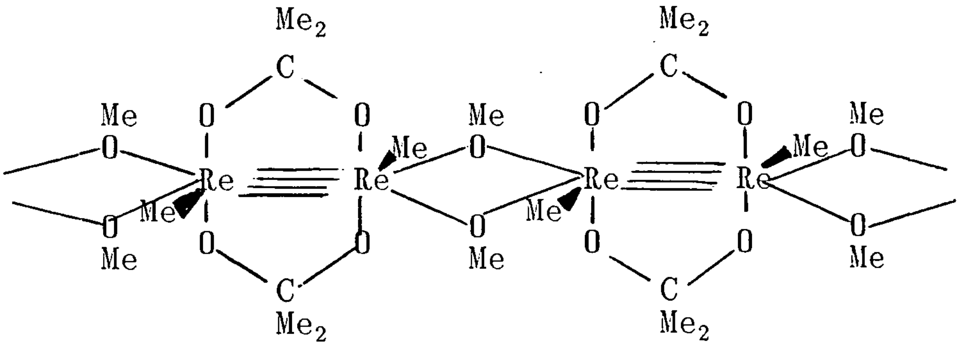
Wilkinson et al [154] have prepared and studied the reaction of $ReOX_2(OEt)(PPh_3)$:

$$\begin{tikzcd}
HReO_4 \arrow[r, "A{,}B"'] & ReOX_2(OEt)(PPh_3)_2 \arrow[d, shift left, "D"] \\
 & ReOX_3(PPh_3)_2 \arrow[u, shift left, "C"]
\end{tikzcd}$$

A EtOH, PPh_3, hydrohalic acid (X=Br orI);using MeOH→OMe complex.
B EtOH, PPh_3, hydrazine hydrochloride (X= Cl)
C Ethanol (X=Cl, Br or I)
D CH_2Cl_2 solution, hydrochloric acid (X=Cl, Br or I)

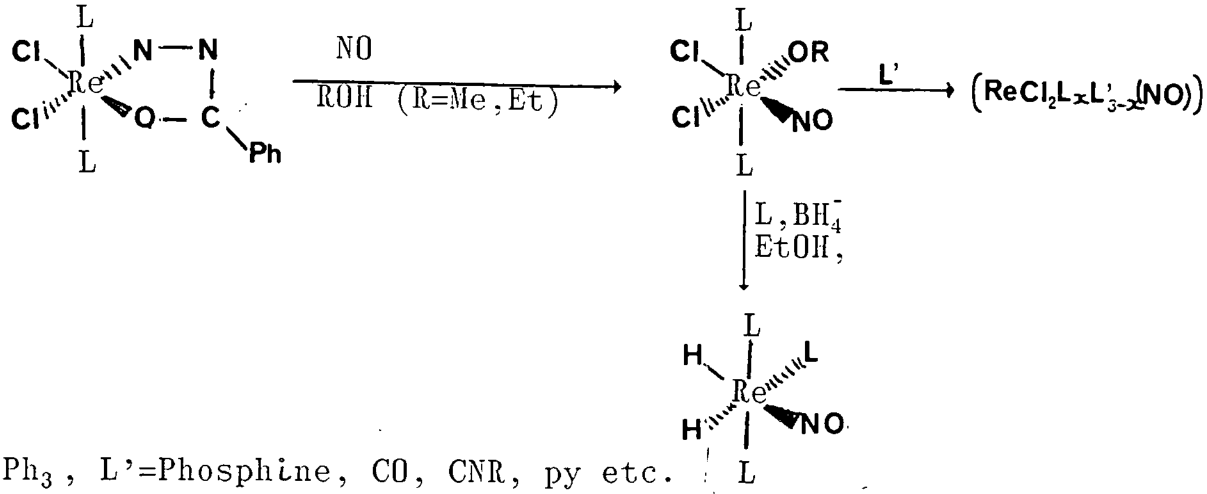
Reactions between the quadruply Re-Re bonded complex $Re_2(O_2CR_2)_2X_4L$, where L = H_2O, DMF or DMSO, and PPh_3 in refluxing alcohol ROH, where R = Me, Et, ^nPr, ^iPr, yields red crystalline, diamagnetic complexes of stoichiometry $Re_2(OR)_2X_4(PPh_3)_2$. The ethoxide derivative has been characterized by x-ray diffraction and shown to possess the novel structure $(EtO)_2Cl_2Re.ReCl_2(PPh_3)_2$. This is best described as a Re(IV)-Re(II) complex that has been derived from the Re(III)-Re(III) core by an intramolecular disproportionation. The Re-Re bond distance is 2.231Å and is a quadruple bond, but one component has dative character (ReII→ReIV). The alkoxide ligands are good π donors and this will help offset some of the formal charge separation. The Re-O bonds are very short (1.88Å) and a strong O→Re donation takes place, mainly from one oxygen p_π orbital (one whose nodal plane is the C-O-Re plane), since PPh_3 is too large to allow the ethyl groups to move out (M-O-C angle is not opened as is usual with strong alkoxide π bonding).

Warming $Re_2Me_2(O_2CMe_2)$ with methanol [155] gave a mauve, insoluble powder of stoichiometry $\{ReMe(OMe)(O_2CMe_2)\}_n$ which has the probable structure:



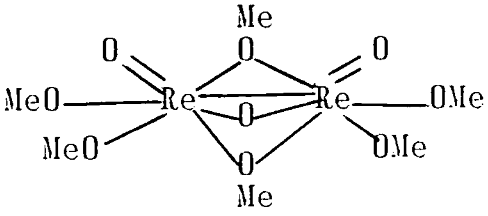
Ethanolic solutions of $[\{ReCl_2(CO)_2(NO)\}_2]$ may be reduced with zinc in the presence of carbon monoxide to yield the ethoxy-bridged dimer $[Re_2(\mu OEt)_3(CO)_5NO]$, which is isoelectronic with the well-known anions $[Re_2(\mu OR)_3(CO)_6]^-$.

The complex $[ReCl_2(OMe)(PPh_3)_2NO]$ has proved to be a useful precursor [156]:



L=PPh_3, L'=Phosphine, CO, CNR, py etc.

$ReOCl_4$ reacts with methanol in the presence of amines to give the unusual alkoxy compound $(MeO)_2(O)Re(\mu O)(\mu OMe)_2ReO(OMe)_2$ (9), whereas $LiOBu^t$ gives $ReO(OBu^t)_4$ (10) and $LiOPr^i$ gives an unusual dimeric species $Li[ReO(OPr^i)_5]LiCl(THF)_2$ (11). The interaction of phenol in the presence of trimethylphosphine leads to the compound trans-$(Me_3P)_2Re(OPh)_4$ (12) [157,158]. From NMR, IR and x-ray studies the structure of (9) has been determined as:



The trimeric rhenium cluster alkoxide $Re_3Cl_3(OBu^t)_6$ has also been synthesized [159].

Iron, Ruthenium and Osmium

The simple alkoxides of iron are dealt with in refs. [86, 160-166]. No simple alkoxides of ruthenium or osmium have been reported to date.

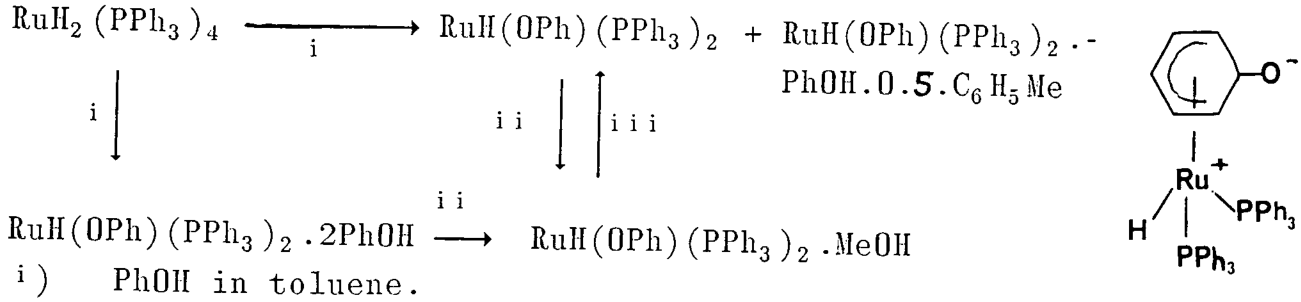
Alkoxy Derivatives of Iron

A series of complexes of iron(II) alkoxides and aryloxides with 2,2 bipyridine (L), having formulae $Fe(OC_6H_4X)_2L_n$ and $Fe(OR)_2L_n$, have been prepared by reaction of diethylbis(2,2 bipyridine)iron(II) with p-substituted phenols (substituent X = H,Me,Ph,Cl,CN and NO_2) and alcohols ROH (R = Me,Et,^{i}Pr, H_2CPh). Interaction of these complexes with acyl and alkyl halides yield the corresponding esters and ethers [167]. The number of coordinated bipy ligands depends on the electron withdrawing or donating properties of the p-substituent on the phenoxy ligand. The ^1H NMR spectra show that the phenoxy ligands are bridging and in cis positions for steric reasons. These complexes were found to be very air sensitive but thermally stable.

Alkoxy Derivatives of Ruthenium and Osmium

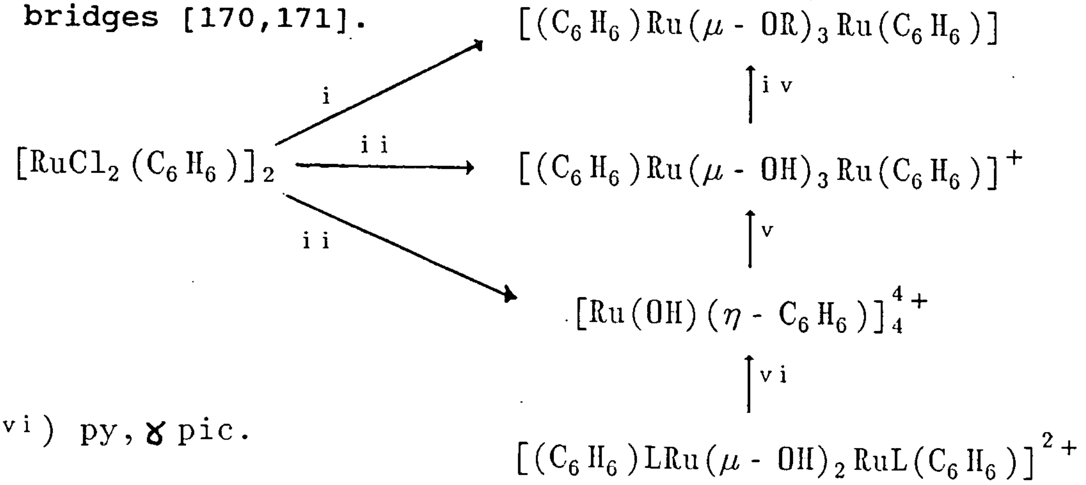
All the insoluble alkoxy derivatives of ruthenium and osmium are either binuclear (with rather close resemblance to each other) or polynuclear (with marked differences among themselves) [168].

Dihydrotetrakistriphenylruthenium(II) reacts with phenol to give the neutral complex $RuH(C_6H_5O)(PPh_3)_2$. $C_6H_5O^-$ can be considered to be bound as $\eta 6$ phenoxo or, probably more realistically, as a η^5 oxacyclohexadienyl ligand. The bonded nature of the phenoxide ion is confirmed by IR, NMR and x-ray structural data [169]. Different products may be isolated depending on the reaction conditions and on the recrystallization process:



i) PhOH in toluene.
ii) Recrystallisation from methanol.
iii) Recrystalisation from dichloromethane/petroleum.

Treatment of $[RuCl_2(\eta C_6H_6)]_2$ with sodium alkoxide in alcoholic solvents affords the yellow solids $[(C_6H_6)Ru(OR)_3Ru(C_6H_6)]^+$ (R = Et,Me), with triple alkoxide bridges [170,171].

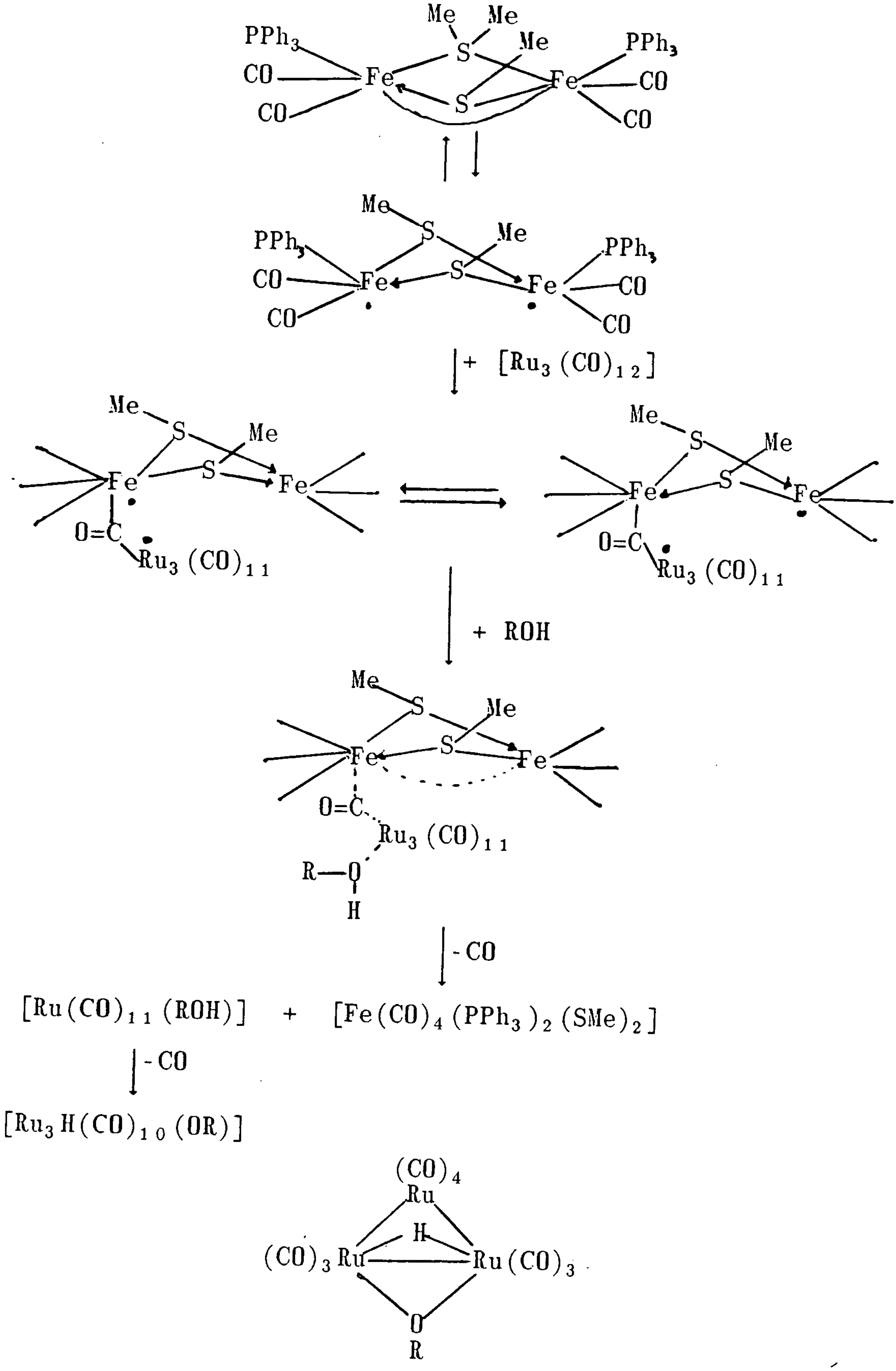


vi) py, γ pic.

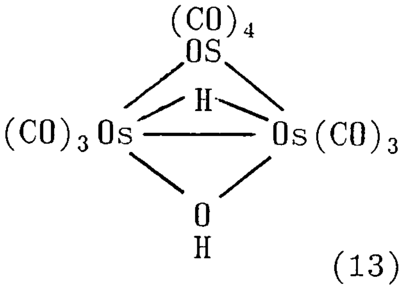
i) OR^-, ii) excess OH^-, iii) CO_3^{2-}, iv) ROH reflux v) OH^-

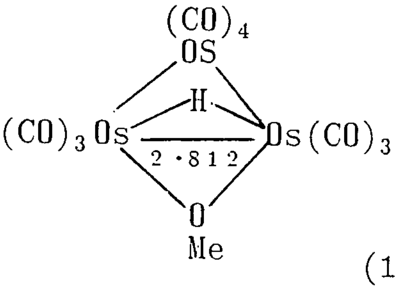
The reductive carbonylation of methanolic solutions of hydrated $RuCl_3$ in the presence of zinc gives $[Ru(CO)_{12}]$ as the major product. After separation of this product the mother liquors afford several other complexes, the major ones being $[H_2Ru_4(CO)_{12}]$ and $[H_4Ru_4(CO)_{12}]$ [172]. Further separation by TLC gave at least ten components, ranging in colour from yellow to purple, of which the tetranuclear complexes $[Ru_4(CO)_{10}Cl_2(OMe)_2]$, $[Ru_4(CO)_{10}Cl(OMe)_3]$, $[Ru_4(CO)_{10}Cl_2(OH)(OMe)]$ and $[Ru_4(CO)_{10}Cl_2(OH)_2]$ and $[Ru_4(CO)_{10}Cl(OH)(OMe)_2]$ were characterized by mass spectrometry. In ethanol $[Ru_4(CO)_{10}Cl_2(OH)(OEt)]$, $[Ru_4(CO)_{10}Cl_2(OH)_2]$ and $[Ru_4(CO)_{10}Cl(OH)(OEt)_2]$ were identified. The structures are not known; the alkoxy ligands may act as 1 or 3 electron donors.

The use of dinuclear carbonyl iron complexes $[FeCp_2(CO)_4]$ and $[Fe_2(CO)_4(PPh_3)_2(SMe)_2]$ as catalysts in reactions of carbon monoxide replacement by the weak nucleophilic molecules ROH ($R = Me, Et, Pr^n, Bu^n$) allows isolation of a series of derivatives $[Ru_3(\mu H)(CO)_{10}(\mu OR)]$, previously inaccessible by thermal routes [173]. Yields follow the order $Me < Et < Pr^n < Bu^n$, which supports the mechanism below. The important step related to the formation of the $[Ru_3(CO)_{11}(ROH)]$ adduct is clearly the nucleophilicity of the alcohol employed, which shows the same order as the product yields. The formation of the final compound is accounted for by a simple internal oxidative-addition, coupled with the elimination of a CO ligand.

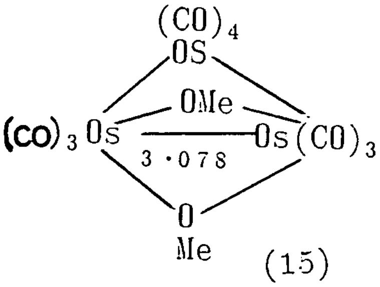

Me
Me
Me
PPh3
PPh3
CO
CO
CO
CO
Fe
Fe
S
S
+ [Ru3 (CO)12]
O=C
Ru3 (CO)11
+ ROH
R—O
H
- CO
[Ru(CO)11 (ROH)] + [Fe(CO)4 (PPh3)2 (SMe)2]
- CO
[Ru3 H(CO)10 (OR)]
(CO)4
Ru
H
(CO)3 Ru
Ru(CO)3
O
R

OsO_4 reacts with carbon monoxide in methanolic solution to give the trinuclear complexes $HOs_2(CO)_{10}(OH)$, $HOs_3(CO)_{10}(OMe)$ and $Os_3(CO)_{10}(OMe)_2$ [176]. The structures are believed to be as shown below:


(13)



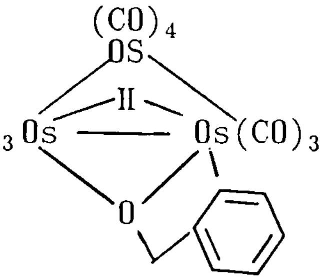
(14)



(15)

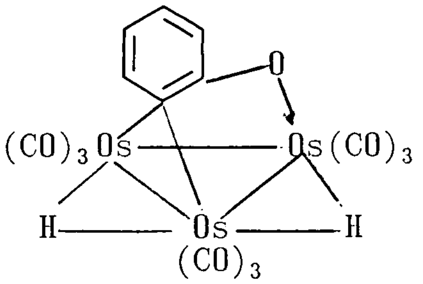
The short Os-Os distance of 2.812Å in (14) implies the existance of a metal-metal bond with the methoxy group serving as a three electron donor. The bridged osmium atoms in complex (15) are not mutually bonded, as predicted on the basis of electron counting [175].

Alcohols with aromatic substituents react with $Os_3(CO)_{12}$ initially to produce the expected hydrido-aryloxy bridged species, but with further heating ortho activation of the aromatic C-H bonds occurs. For example, thermolysis of $[Os_3(H)(\mu OCH_2Ph)(CO)_{10}]$ converts it to $[Os_3(H)_2(\mu OCH_2C_6H_4)(CO)_9]$, (16), which contains a five-membered metallacyclic ring [176].


(16)

In contrast, $[Os_3(H)(\mu OPh)(CO)_{10}]$ is converted into

$[Os_3(H)_2(\mu OC_6H_4)(CO)_9]$ [177], analogous to $[Os_3(H)_2(OC_6H_3CH_2Ph)(CO)_9]$ which has been structurally characterized [178]. This complex (17) contains a five-membered metallacyclic ring also, but this ring contains two metal atoms.



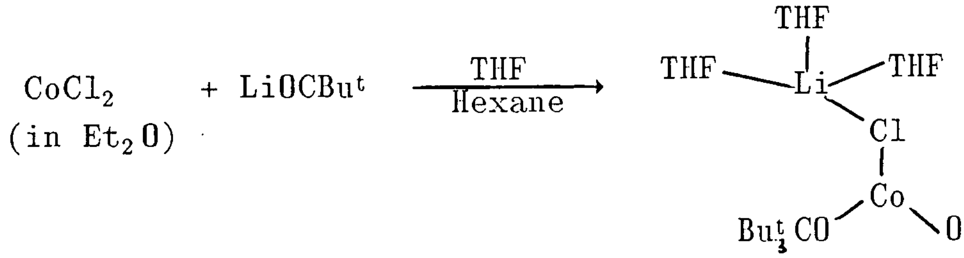
(17)

Cobalt, Rhodium and Iridium

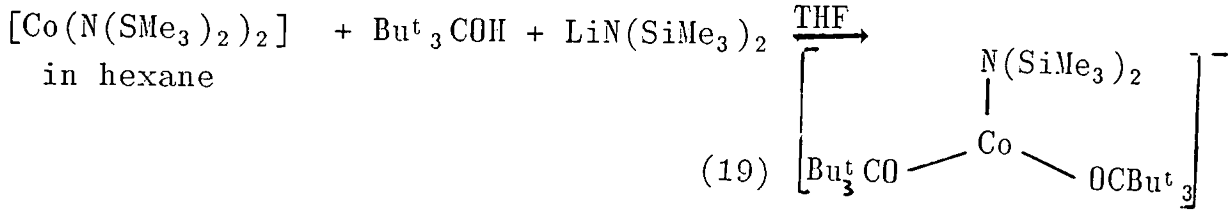
Winter has studied the simple alkoxides of cobalt extensively, including their electronic spectra and magnetic properties [179]. Other studies are to be found in refs. [160,180-184].

Alkoxy Derivatives of Cobalt

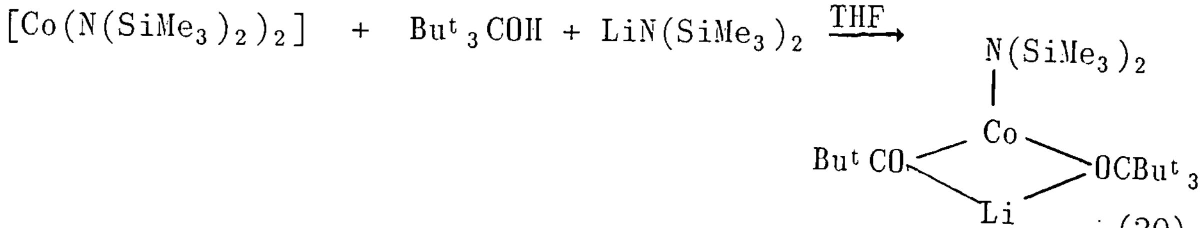
Sigel et al [185] have prepared and characterized $[Co(Cl)(OCBu^{t}{}_3)_2.Li(THF)]$ (18), $[Li(THF)_{4.5}][Co[N(SiMe_3)_2](OCBu^{t}{}_3)_2]$ (19) and $[Li\{Co[N(SiMe_3)_2]_2(OCBu^{t}{}_3)_2\}]$ (20).In all these complexes Co(II) has the rare distorted trigonal planar geometry due to the size of the substituents. Other features of interest involve the inclusion of lithium chloride in (18), the solvated lithium cation in (19) and agostic interactions between the ligand methyl groups and cobalt or lithium in (18)-(20). The complexes are exceptionally air sensitive.



(18)



(19)



(20)

Cobalt alkoxy derivatives are involved in the catalysis of the carboxylation of olefins, in particular that of butadiene to give methyl-3-pentanoate, a potential precursor for dimethyladipate and nylon-66 [186].

Alkoxy Derivatives of Rhodium and Iridium

The alkoxide chemistry of rhodium and iridium has been studied mainly for the +1 oxidation state, obtained initially by reduction of their salts in the +3 states, and stabilized by ligation with acceptor ligands such as cyanide, phosphine, carbon monoxide, olefin and diolefin. Iridium doesnot appear to exist in the +2 state and triply-bridged phenoxy derivatives of Rh(II) only have been described [168].

Reaction of $[\{RhCl(CO)_2\}_2]$ with sodium methoxide and methanol in benzene or hexane solution between 0 and 30°C yields $[\{Rh(OMe)(CO)_2\}]$, where OMe groups have replaced Cl as the bridging ligands. The product is unstable and must be prepared under anhydrous conditions as traces of water lead to $[Rh_4(CO)_{12}]$ [187].

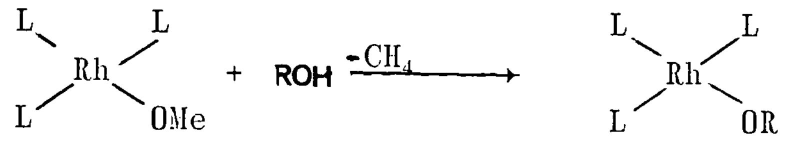
More stable, monomeric compounds can be prepared:

$$Rh_2(CO)_4(OR)_2 + 4PPh_3 \longrightarrow 2Rh(CO)(PPh_3)_2(OR) + 2CO$$

$$R = nC_3H_7,\ C_6H_5,\ p\ ClC_6H_4$$

The IR spectra show a band almost always appearing as a doublet and the intensity changing with temperature and time. This has been attributed to a syn—anti equilibrium, i.e. both Me groups above, or one above and one below, the Rh_2O_2 plane.

$(PPh_3)_3RhR$ (R = Me,Ph) reacts with phenol to yield $(PPh_3)_3RhOPh$ and an alkane RH. The solid is reddish-brown and easily loses one PPh_3 ligand when stirred under petroleum to give $[Rh(OPh)(PPH_3)_2]$, which is most likely monomeric and contains bonded OPh [169,188]. In contrast, treatment of a toluene solution of $(PMe_3)_3RhMe$ (21) with one equivalent of the appropriate alcohol at room temperature gives a bright yellow alkoxide complex in good yield: none of the corresponding bonded phenoxide complexes were found (formation probably requires loss of a strongly bound PMe_3 ligand).



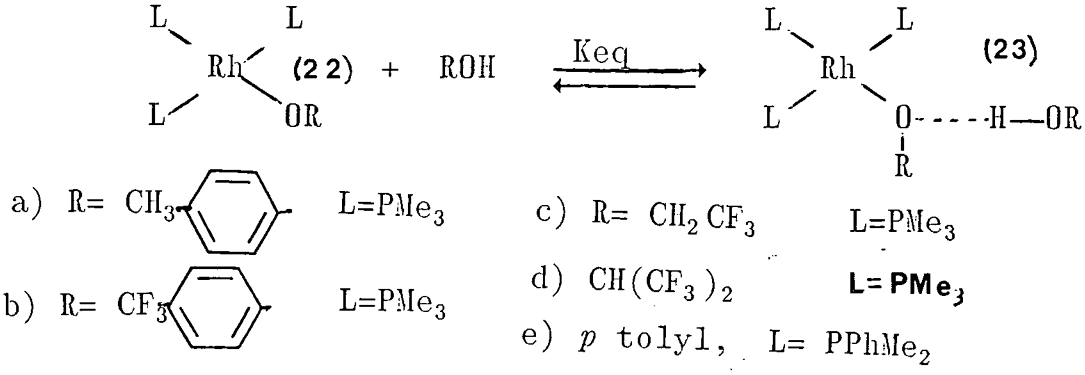
(L=PMe_3) Square planar Rh(I)

(21) (22)

Four $(PMe_3)_3RhOR$ complexes have been prepared in this way, containing p-methylphenoxy, p(trifluoromethyl)phenoxy, trifluoroethoxy and hexafluoroisopropoxy groups.X-ray diffraction indicates little or no interactions of the alkoxide ligands with the metal.

Alternative synthetic pathways to the alkoxide complexes include reaction of $[(COD)Rh(Otol)]_3$ with phosphine (COD = 1,5 cyclooctadiene; tol = $pCH_3C_6H_4$) and $(PMe_3)_3Rh^+PF_6^-$ with KOR (R = $pCH_3C_6H_4$, CH_2CF_3).

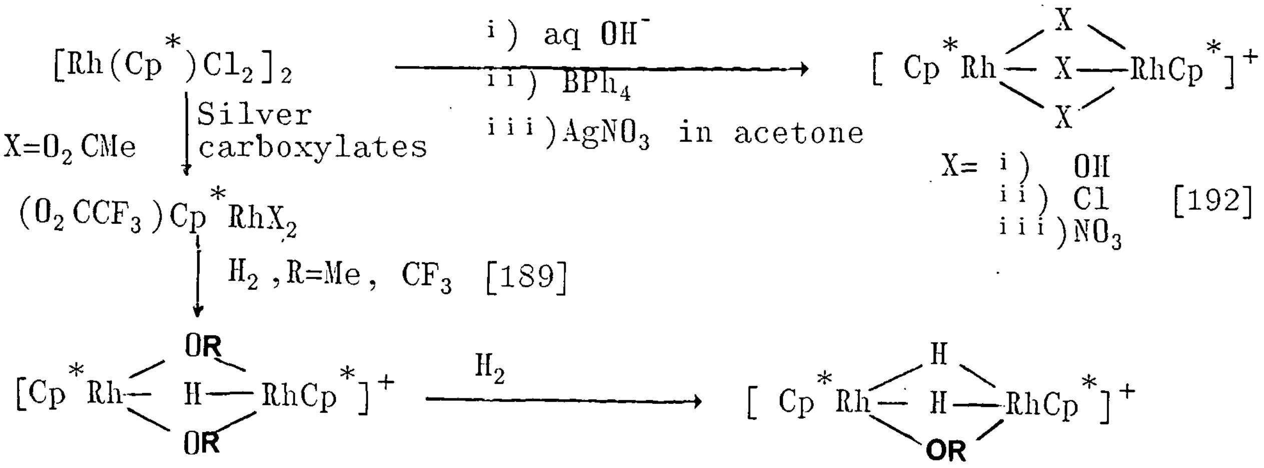
One or two equivalents of ROH or p-cresol with complex (21), or reaction of complex (22) with a single equivalent, yields a hydrogen bonded species:



The molecule of alcohol is strongly associated with the alkoxide complex, even in solution. The O-H-O linkage is markedly asymmetric, though essentially linear, the hydrogen atom being more closely associated with the molecule of p-cresol than the alkoxide ligand.

Spectroscopic studies show that the equilibrium lies far to the right, implying that the H-bond in (23a) is unusually strong. It is concluded that the hydrogen bonded p-cresol molecule sees the oxygen atom in the rhodium bound alkoxide as a site of unusually high electron density. This suggests that the Rh-O aryloxide bond is strongly polarized, having excess negative charge at oxygen and excess positive charge at rhodium. The results may have important implications for the catalytic carboxylation of olefins, where a proposed step in one possible mechanism involves the insertion of CO into a M-O bond.

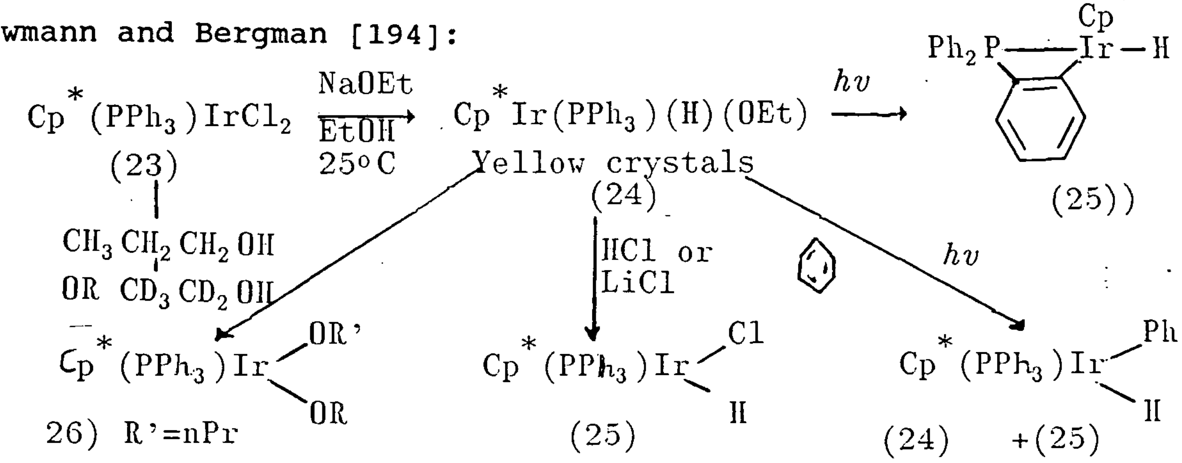
$[RhCp^*Cl_2]_2$ has been used by Maitlis et al [189] to give a series of alkoxy bridged complexes:



These two complexes are active hydrogenation catalysts. Similar iridium complexes have also been obtained [193].

$[Rh\{N(SiMe_3)_2\}(PPh_3)_2]$ and ArOH, where ArO^- is the ambidentate nucleophile 2,6 di-t-butyl-4-methylphenoxide, yield the d^8 complex $[Rh(ArO\eta^5)(PPH_3)_2]$ [192]. The ArO ligand is η^5 [C(2)-C(6)] bonded, i.e. coplanar.

The following reaction sequence has been devised by Newmann and Bergman [194]:

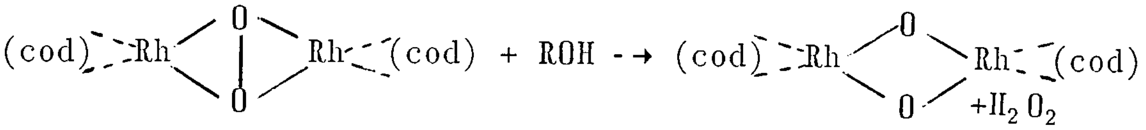


The reactions leading to complexes (24) and (25) are consistent with electrophilic attack on the OR^- ion by the substrate. Further indication of the reaction of OR^- is provided by the exchange with other alcohols (26). Note that no hydride loss occurs even in protic solvents.

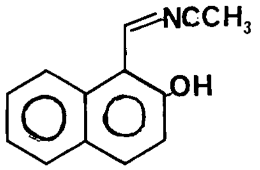
$[(COD)IrCl]_2$ and the rhodium analogue has successfully been used for the synthesis of the methoxy and higher alkoxy derivatives, including phenoxy [168]:

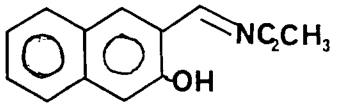
$$[(cod)IrCl]_2 \xrightarrow[ROH]{Na_2CO_3} [(cod)Ir(OR)]_2 \qquad R = Me, Et, Pr^n, Pr^i, Bu^t, Bu^i, C_8H_{17}, Ph.$$

$[(COD)RhCl]_2$ and KO_2 react to give $[(COD)Rh]_2O_2$, which is used in the synthesis of the alkoxy derivatives below:



Rhodium and iridium complexes have been used as catalysts for various reactions. $[(COD)Ir(OMe)_2]$ in the presence of Schiff bases:





catalyses the transfer of hydrogen from ^iPrOH to cyclohexane or acetophenone [195]. $[(COD)Rh(OMe)]_2$ has been used as a catalyst for the carbonylation of methanol to acetic acid [196]. Trans $ROIr(CO)(PPh_3)_2$ (R = Me,^{n}Pr,Ph) has been carbonylated to give a carboalkoxy complex $ROC(O)Ir(CO)_2(PPh_3)_2$. This offers the possibility for reaction of alkenes or alkynes with M-O containing groups [197-199].

Nickel, Palladium and Platinum

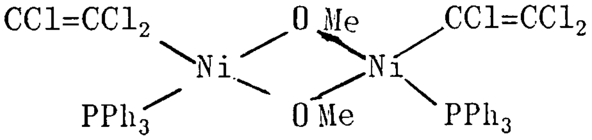
Work relating to the synthesis and properties of the simple alkoxides is to be found in refs. [160,200-206].

Alkoxy Derivatives of Nickel

Winter has prepared a number of halomethoxy derivatives of formula Ni(OMe)X by reaction of NiX_2 (X = Cl,Br,I) with sodium methoxide. With LiOMe nickel (II) chloride yields $Ni(OMe)_4Cl_2$ on refluxing for several minutes, whereas concentrated solutions yield $Ni_3(OMe)_5Cl$. Similarly with the bromide and iodide [201].

Complexes of the type $[LNi(Me)X_2]$, where L = PMe_3, X = OH,OMe,OEt,OPh,$OC_6H_4CH_3$-p, have been prepared [207] and the position of equilibrium between the cis and trans isomers determined from low temperature ^1H NMR.

$[NiRCl(PPh_3)_2]$ complexes, where R = C_6F_5,$CCl{=}CCl_2$, react with sodium methoxide to yield bridging methoxy compounds $[\{NiR(\mu OMe)(PPh_3)_2\}_2]$ as red crystals [208] which are extremely air sensitive and thermally unstable.



The alkoxy derivatives of $[\{NiX(\eta^3 \text{ allyl})\}_2]$ complexes have been prepared and found to undergo spontaneous disproportionation [209]:

$$[\{NiOR(\eta^3 C_3H_5)\}_2] \longrightarrow [Ni(\eta^3 C_3H_5)_2] + Ni(OR)_2$$

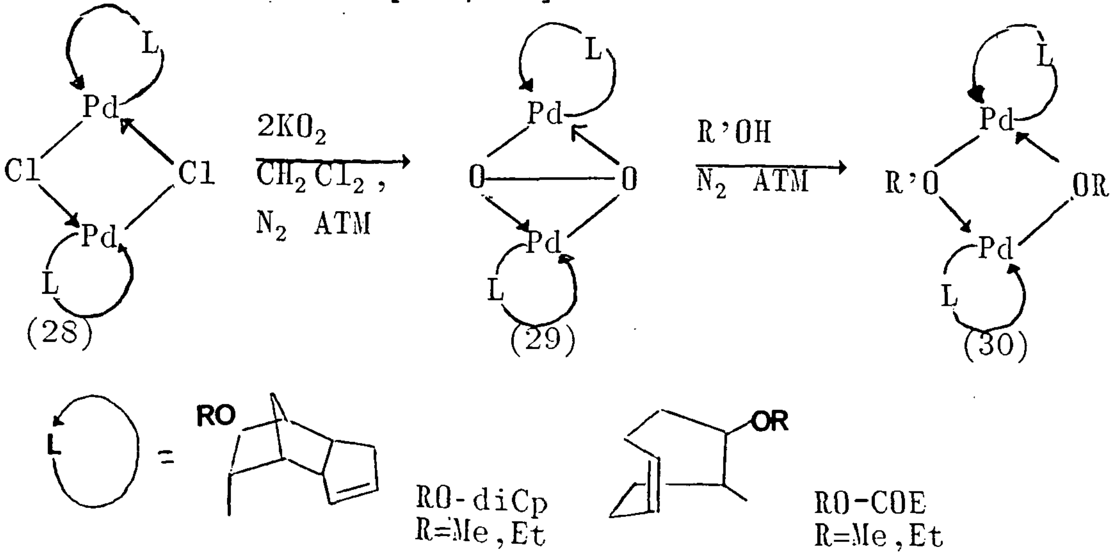
R=Me , η^3 allyl $=\eta^3 C_3H_5$,$2MeC_3H_4$,$2PhC_3H_4$, R =OPh , η^3 allyl$=\eta^3 C_3H_5$

Alkoxy Derivatives of Palladium and Platinum

Transition metal d^8 complexes containing metal-oxygen bonds have been reported to play an important role as intermediates in synthetic reactions, particularly in catalytic processes e.g. hydration of nitriles and oxidation of ethylene and alcohols. Although some nonbridging hydroxo compounds of the $5d^8$ and $6d^8$ metals have been isolated, until 1976 only one alkoxo complex of palladium or platinum was known, Pt(OMe)(cyclohexenyl)($PH_2PCH_2CH_2PPh_2$) [210].This was obtained by reacting the cyclohexene complex with methanol.

Synthesis of $Pd_2(\mu OMe)_2(F_6acac)_2$ by reaction of $Pd(F_6acac)_2$ with methanol at room temperature has been reported [213,214]. Efforts to prepare the higher homologues failed, which might be ascribed to the presence of abstractable hydrogen atoms in the alkoxy groups.

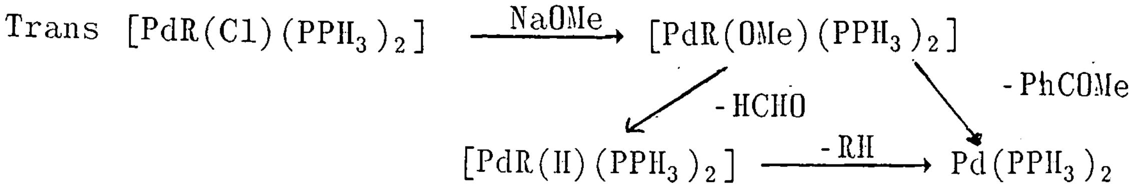
Binuclear alkoxy-bridged palladium products (30) have been obtained by reaction of methanol with dioxygen-bridged complexes (29), which are in turn synthesized by reaction of the corresponding dichloro-bridged Pd(II) complex (28) with KO_2 in dichloromethane [215,216].



The methoxy-bridged complexes are unstable in benzene solution and decompose on heating to 30-40°C to give metallic palladium. In the solid state the decomposition takes place in one day under dry nitrogen. The ethoxy derivative is even less stable. The methoxy- and ethoxy-bridged complexes readily exchange OR groups with ethanol and methanol respectively. Complexes of type (30) have not been prepared with bulky R groups.

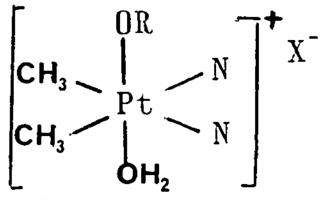
The first moisture stable mixed methoxy and chloro-bridged dinuclear Pt(II) and Pd(II) [211] complexes $M_2(\mu Cl)(\mu OMe)(^tBu_2PCMe_2CH_2)_2$ have been isolated by the reaction of the corresponding chloro-bridged dinuclear complexes $M_2(Cl)_2(^tBu_2PCMe_2CH_2)_2$ suspended in methanol with an equimolar amount of sodium hydroxide at 40°C. The corresponding reaction of $(COD)PtCl_2$ (COD = 1,5 cyclooctadiene) with two equivalents of sodium hydroxide in aqueous methanol yields the methoxy-bridged complex $[Pt(\mu OMe)(C_8H_{12}OMe)]_2$ [212]. The methoxy bridges are cleaved by tertiary phosphines (L) to give mononuclear complexes $(C_8H_{12}OMe)Pt(OMe)L$.

In order to elucidate the factors governing the stability and nature of σ Pt-OR bonds a series of square planar complexes, cis and trans $Pt(OMe)(R)L_2$ ($R = CF_3, CH_2CN, CH_2CF_3$; $L_2 = 2PPh_3$,diphosphine) have been prepared as colourless products in high yields by metathesis of $PtCl(R)L_2$ or $[Pt(R)L_2]BF_4$ with sodium methoxide slightly above room temperature in an anhydrous benzene-methanol mixture [210]. Success in preparing these compounds seems to be related to the nature of the alkyl ligand R, a more electronegative R group will increase the effective positive charge on the metal and consequently the electron density on the methoxy group will decrease, increasing the covalency of the Pt-OMe bond. Conversion to the corresponding hydroxides occurs with water. Pt-O bonds in these complexes undergo facile insertion of CO,COS,CS_2 and SO_2 [217]. Similar reactions can be effected with palladium compounds:



The relative instability of the palladium analogues is shown by the formation of '$Pd(PPH_3)_2$'; the Pd(III) complexes are less stable than those of Pt(I) and (II).

Complexes of the type $[Pt(II)Me_2(\widehat{NN})]$ ($\widehat{NN}$ = 2,2 bipyridine or 1,10 phenanthroline) react with alcohols ROH (R = Me,Et,^{i}Pr) to give alkoxy compounds $[PtMe_2(OR)(\widehat{NN})(OH_2)]^+$ OH^-. These compounds are partly characterized by conversion to the derivatives $[PtMe_2(OR)(\widehat{NN})(OH_2)^+X^-$ (X = PF_6,ClO_4,BPh_4) and to $[PtMe_2(OMe)Cl(phen)]$ (R = Me and $\widehat{NN}$ = phen). The alkoxy Pt(IV) bond is inert to solvation with alcohols, water and dilute perchloric acid [218].



New cis Pt(II) complexes have been synthesized incorporating the chelating dianion of perfluoropinacol $[-OC(CF_3)_2C(CF_3)_2O-]^{2-}$, PFP, in conjunction with phosphine and thioether coligands of the general formula $(PFP)PtL_2$ (L = PMe_3,PMe_2Ph,$PMePh_2$,PPh_3,SMe_2,MeSEt,SEt_2). They are prepared as colourless or pale yellow crystals from the reaction of cis-$PtCl_2(PMe_3)_2$ and HPFP in dichloromethane solution [220]. Among the important reactions of alkoxy complexes of transition metals in low oxidation states are those that involve use of palladium catalysts to effect conversion of alkenes, carbon monoxide and methanol to esters [219-223]. IR and NMR studies are consistent with square planar, 16 electron metal complexes, the CO stretching frequency indicating that PhO^- is a weaker electron donor than RO^-, as expected.

Copper, Silver and Gold

Relatively little work has been carried out on this group of metals, and silver has no reported simple alkoxides or alkoxy derivatives. The simple alkoxides of copper are reported in refs. [5,181,224-234].

Alkoxy Derivatives of Copper

It has been reported that coordinated diphenoxo derivatives have been obtained by the reactions:

$$CuCl_2(bipy) \quad + \quad 2NaOPh \quad \xrightarrow{THF} \quad Cu(OPh)_2(bipy) \quad + \quad NaCl$$

brown complex
soluble in THF.

$$CuCl_2(en) \quad + \quad 2Na(OPh).PhOH \quad \xrightarrow{THF} \quad Cu(OPh)_2(en).PhOH + NaCl$$

green complex sparingly
soluble in THF.

Both complexes are highly moisture sensitive.

$Cu(OPh)_2(en).PhOH$ has been shown by x-ray diffraction to be a centrosymmetric phenoxy-bridged dimer with terminal phenoxy and ethylenediamine (en) groups and hydrogen bonded phenol molecules [235]. The copper atoms are five-coordinate, and the coordination geometry is that of a distorted square pyramid.

Copper (I) alkoxides $ROCu(PPh_3)_2$ (R = Et, $PhCH_2$) react with CO_2 to give products corresponding in composition to $ROCO_2Cu(PPh_3)_2$ [236].

$^tBuOCuCO$ reacts with $^nBu_3P$, $(MeO)_3P$ or ^tBuNC in benzene to give a phosphine or isocyanide complex. The latter is obtained as yellow crystals. There is no decarbonylation on adding nitrogen donor ligands such as pyridine. The inertness of Cu(I)-OR towards insertion of CO and isocyanide contrasts with the high reactivity of the Cu(II)-OR bond [238].

$Cu(OBu^t)(PEt_3)$ metallates cyclopentadiene at -78°C, enabling the synthesis of cyclopentadienylcopper-ligand complexes [233]:

$$[Cu(OBu^t)(PEt_3)] + C_5H_6 \longrightarrow [Cu(\eta C_5H_5)(PEt_3)] + HOBu^t$$

The complexes $[Cu(2NH_2py)(OR)]$ (R = H,Me,Et,Pr or pentyl; $2NH_2py$ = 2aminopyridine) and [Cu(pd)OMe] (pd = pentane-2,4-dionato) are obtained from the [Cu(L)OMe] complex by treatment with sodium hydroxide in refluxing methanol and then conversion of the methoxide to the desired alkoxide by recrystallization from the appropriate alcohol [237]. The [Cu(pd)OMe] complex is a blue, dimeric solid with bridging methoxy groups. All decompose slowly on exposure to the atmosphere.

Alkoxy Derivatives of Gold

The monomeric gold (I) alkoxide Ph_3PAuOR (R = ^tBu (31), $2,4,6\,^tBu_3C_6H_2$ (32)) can be isolated as white microcrystalline solids from the reaction of sodium alkoxide with Ph_3PAuCl in THF [239]. The reaction of the three equivalents of $Ph_3PAuOBu^t$ with $ReH_5(PMe_2Ph)_3$ gives $(Me_2PhP)_3Re_2AuPPh_3)_3$. With (32) the product is $[(Me_2PhP)_3ReH_3(AuPPh_3)_3]^+[O\ 2,4,6^tBu_3C_6H_2]^-$.

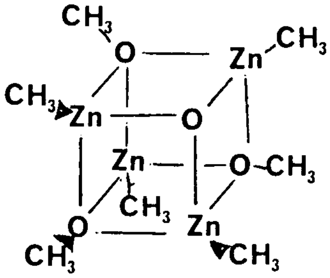
Caulton [240] has formed heterometallic polyhydride rafts using $[Ph_3PAuOBu^t]$ with $[Re_2H_8(PMe_2Ph)_4]$.

Zinc, Cadmium and Mercury

Work relating to the simple alkoxides of zinc is collected in refs. [241-244]. Binary alkoxides of cadmium and mercury have not been reported.

Alkoxy Derivatives of Zinc [4]

Slow addition of methanol to Me_2Zn in hexane at -70°C yields methylzincmethoxide [245], which is tetrameric and has a cubic structure [246]. This method can be extended to other alkoxides RZnOR [247], the reactivity of the Zn-C bond towards acidic protons being very high.



When very bulky groups are present the compounds form dimeric or trimeric aggregates which contain coordinatively unsaturated zinc, e.g. dimeric phenylzinctriphenylmethoxide [248] and trimeric t-butylzinc-t-butoxide [249]. The degree of association is also affected by the electronegativity of the group bound to zinc via oxygen. When an electron withdrawing group is introduced, the donating capacity of the oxygen atom will be smaller, resulting in weaker Zn-O coordinate bonds. This doesnot always lead to lower association, e.g. ethylzincphenoxide is still a tetramer, but in extreme cases dimers are also found, e.g. ethylzincpentafluorophenoxide [249]. The tetrameric complexes contain coordinatively saturated zinc and donot readily react with coordinating agents, since this would require cleavage of the intramolecular Zn-O coordinate bonds. Organozinc alkoxides derived from saturated, straight chain alcohols do not react with any complexing agent, indicating that the intramolecular coordinate bonds are very strong. Where zinc is coordinatively unsaturated (dimeric or trimeric complexes),or when the electron donating power of the oxygen atoms of the alkoxide ligands is small, e.g. aryloxides, complex formation will occur. Table 7 gives details of the coordination behaviour of organozinc alkoxides.

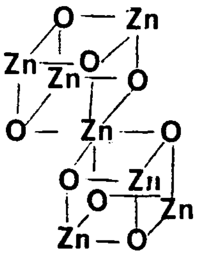
TABLE 7 COORIDINATION BEHAVIOUR OF ORGANO ZINC OXYGEN COMPOUNDS

Compound	Degree of association in benzene	Stoichiometry of compound with		Ref
		py	TMEA	
MeZnOMe	4	no complexes	formed	[247]
Bu^tZnOBu^t	3	1:1	no complex	[249]
$PhZnOCPh_3$	2	—	—	[248]
EtZnOPh	4	2:2	2:1	[249]
$EtZnOC_6F_5$	2	2:2	1:1	[249]

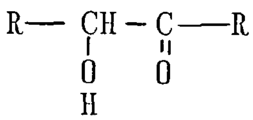
Most organozinc alkoxides are stable species,but redistribution equilibria can occur:

$$^{n}R_2Zn \quad + \quad {}^{m}ZnX_2 \rightleftharpoons R_{2n}Zn_{n+m}X_{2m}$$

As a result of the presence of different species in solution recombination reactions may occur, leading to aggregate formation, as for example in solutions of methylzincmethoxide from which $Me_6Zn_7(OMe)_8$ has been isolated [250]. The ethyl analogue is also known, $Et_7Zn_7(OMe)_8$ [251]. Both exist as two distorted Zn_4O_4 cubes sharing a zinc atom.



Dimethylzinc reacts with triisopropylvanadate to give $MeZn(OPr^i)$ as one of the products [252] and it has been found that organozinc compounds will react with carbon monoxide in the presence of $KOBu^t$:



$$2R_2Zn \quad + \quad 2KOBu^t \qquad 2K^+(R_2ZnOBu^t)^- \xrightarrow[ii)\,H_2O]{i)\ CO} R—\underset{\substack{|\\O\\H}}{CH}-\underset{\substack{\|\\O}}{C}—R$$

Alkoxy Derivatives of Cadmium

A few compounds of this type have been prepared by reaction of $CdMe_2$ with alcohols [253]. The mechanism of the protonolysis of $CdEt_2$ with alcohols in various solvents has been investigated [254].

MeCd(OMe) is insoluble in benzene but the ethoxide, isopropoxide, and phenoxide are soluble and associated into tetramers like their zinc analogues. Solid MeCdOMe is isomorphous with MeZnOMe, suggesting that it is also a tetramer. The methyl cadmium alkoxides are structurally identical to their zinc counterparts, containing distorted cubic Cd_4O_4 units. Their associative behaviour is also similar, as discovered by a Cd NMR study [255]. $MeCd(OBu^t)$ is probably dimeric, unlike the zinc analogue, although no great steric interference should be present in a tetrameric structure. Possible evidence of a tetramer has been found in NMR studies.

Only the phenoxide reacts with pyridine to give a dimeric complex $(MeCdOPh.py)_2$, which is partially dissociated in benzene solution.

Table 8 gives details of the association behaviour of cadmium alkoxy derivatives.

TABLE 8 ASSCIATION BEHAVIOUR OF ORGANOCADMIUM-OXYGEN COMPOUNDS

Compound	Degree of association in benzene solution	Ref
MeCdOMe	Insoluble; very likely tetrameric	[254]
MeCdOEt	4	[254]
$MeCdOPr^i$	4	[254]
$MeCdOBu^t$	2 (tetrameric association in nmr studies)	[254]
MeCdOPh	4	[254]

Alkoxy Derivatives of Mercury

Examples of the methods of preparation of the alkoxides and aryloxides are shown below [256-258]. The alkoxides are reported to be water sensitive.

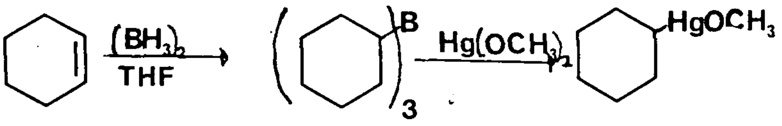
$PhCH_2HgCl + NaOBu^t \xrightarrow{Et_2O} PhCH_2HgOBu^t$

$(PhHg)_2O + (RO)_2CO \longrightarrow 2PhHgOR + CO_2$

$PhHgOCH_3 + ROH \longrightarrow PhHgOR + CH_3OH$

$CH_3HgOAc + ArOH \longrightarrow CH_3HgOAr$

Organoborane compounds have found particular use in recent years and for transfer of secondary alkyl groups from boron the preferred mercury reagents are alkoxides, e.g. $Hg(OMe)_2$ or, better, $HgOBu^t$ [259].



Insertion into the Hg-O bond can take place, e.g. [260]:

$PhHgOR + R'NCO \xrightarrow{CH_2Cl_2} PhHgN(R')CO_2$

80 - 100%

R = alkyl or HgPh

R' = aryl or alkyl

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CHAPTER 3

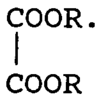
EXPERIMENTAL WORK

Introduction

In this chapter the preparation of alkoxide derivatives of bromopentacarbonylmanganese (I) and of bromotetracarbonyl (triphenylphosphine)manganese (I) are described. The initial study was aimed at obtaining mononuclear manganese alkoxide derivatives according to the following reaction scheme:

$$\begin{tikzcd}
Mn_2(CO)_{10} \arrow[r, "Br_2"] & Mn(CO)_5Br \arrow[r, "ROH", "Et_3N"'] & Mn_3(CO)_9(OR)_3 \arrow[d, "CO"', "\text{High pressure}"] \\
 & & Mn(CO)_5OR
\end{tikzcd}$$

From $Mn(CO)_5OR$ complexes insertion of CO into the Mn-OR bond would give Mn-COOR complexes and possible precursors of



$$\begin{matrix} COOR. \\ | \\ COOR \end{matrix}$$

Oxalate esters provide a route to the higher valued glycol. However, the production of mononuclear alkoxylcarbonyls using CO at high pressures and elevated temperature proved unfruitful and efforts were concentrated on producing alkoxide derivatives under normal laboratory conditions.

The study is divided into three parts. The first section deals with the preparation of $Mn(CO)_5Br$ [1] and $Mn_3(CO)_9(OEt)_3$, the latter using Abel's method [2]. This method was then extended to other alcohols. The second section describes a period of experimental work involving the testing of different bases and solvents to find the best conditions for obtaining good and reliable yields, and the final section then describes the application of this work to producing a wide range of the title compounds.

General Aspects

All reactions were carried out in dry flasks under a continuous flow of N_2, and manipulations were carried out in a glove box under dry N_2, efforts being taken to exclude air and moisture at all times during preparation. Solvents were dried where possible and transferred to the reaction vessel using syringes. Infrared spectra were recorded as nujol mulls using KBr discs or as solutions using a solution cell with CaF_2 windows (path length 0.1mm) on a Perkin-Elmer 457 IR spectrophotometer. The reactions were monitored by taking IR solution spectra over the carbonyl stretching region, 2500-1700 cm^{-1}. Mass spectra were recorded on a A.E.I MS9 mass spectrometer operating at 70 eV. Electron impact and chemical ionization spectra were recorded. In general the CI spectra were used for interpretation, and EI were used where they provided additional information. Proton NMR spectra were recorded on a Bruker HX90E spectrometer at 60MHz. $CDCl_3$ or d_6-acetone solutions were used and TMS was the internal reference. C, H and N analyses were carried out by the departmental microanalyst using a Carlo Erba 1106 Elemental Analyser. Manganese analyses were obtained using atomic absorption spectroscopy and Bromine contents determined by titration with silver (I) ions.

In the following sections, reactions are assigned numbers (in parentheses) for easy reference.

Preparation of $Mn(CO)_5Br$ [1]

$Mn_2(CO)_{10}$ (6.9g) was dissolved in dichloromethane (80 ml). The flask was cooled to 0°C in an ice bath and a solution of bromine (1.26 ml) in dichloromethane (25 ml) added dropwise. The mixture was kept at 0°C for 1 hour with continuous stirring. The solvent was then removed and the orange solid added to water (100 ml) to dissolve any $MnBr_2$. The mixture was agitated and then filtered by suction. The residue was washed with two portions of water (50 ml) and methanol (20 ml). After drying in air the solid was sublimed, small quantities at a time, at 50-60°C (0.1 mmHg). The air-stable, orange crystals were obtained in greater than 90% yields.

IR spectrum: ν(CO) (nujol mull): 2133(m), 2050(w), 2019(s) 2001(w) cm^{-1}

Preparation of $Mn_3(CO)_9(OEt)_{3-}$ [2]

$Mn(CO)_5Br$ (approx. 4 mmole) was dissolved in hexane (10 ml) and triethylamine and ethanol (8 mmole) added. The mixture was then heated to 45°C for 7hrs, with constant stirring. Initially the solution was orange but after a few hours became a deep red colour.

The solution was then cooled and filtered to remove the deposited solid. The filtrate was concentrated to approx. 3 ml and cooled to -20°C. Dark red crystals were obtained which were recrystallized from hexane to give pure tris(tricarbonylethoxomanganese).

$$3Mn(CO)_5Br + 3EtOH + 3Et_3N \longrightarrow Mn_3(CO)_9(OEt)_3 + 6CO + 3[NEt_3H]Br$$

IR spectrum: ν(CO) (hexane solution/literature values): 2063(w), 2034(v.s.), 2030(v.s.), 1974(s), 1962(s), 1954(s), 1938(m), 1930(s), 1903(w) cm^{-1}.

SECTION I

A Reactions of $Mn_3(CO)_9(OEt)_3$ with CO

1. Room temperature, 1 atm. CO pressure

A sample of $Mn_3(CO)_9(OEt)_3$ (few mgs) was dissolved in hexane (10 ml) the flask heated to 55°C and CO gas bubbled slowly through the solution. An IR solution spectrum was taken after an hour, which revealed only the peaks of the starting material. The temperature was raised to 60°C, then 65°C and finally 70°C. IR solution spectra at each temperature showed no change in the peak position, but there is a suggestion of some decomposition to $Mn_2(CO)_{10}$ at 70°C. The solution remained orange in colour and, besides some $Mn_2(CO)_{10}$, it appears that no new products were formed (cf. ref. [1]).

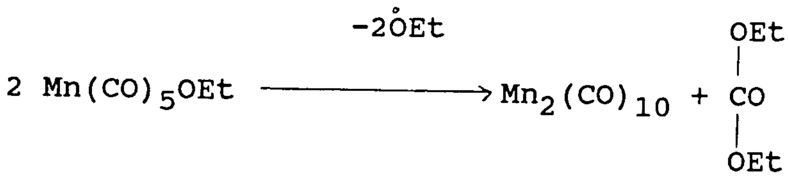
2. Elevated temperature and high CO pressures

Samples of $Mn_3(CO)_9(OEt)_3$ (0.05g) were dissolved in hexane (50ml) and placed in the autoclave. The temperatures, CO pressures and reaction times were varied as shown below, together with the results of IR solution spectra obtained at the end of each experiment.

Temp /°C	Pressure / atm	Time / hr	Outcome (from IR)
55	20	2	x
60	30	3	x $Mn_2(CO)_{10}$
60	60	3	x
70	60	2	x
70-90	60	2	✓ $Mn_2(CO)_{10}$
65-110	30	4	✓ $Mn_2(CO)_{10}$

100	100	1	"
110	60	2	"
120	60	1	"

In the cases where there appeared to be reaction there was also decomposition to $Mn_2(CO)_{10}$, and the attempts to prepare a mononuclear alkoxide by this method were abandoned. A mixture of $Mn(CO)_5$ OEt and $Mn_2(CO)_{10}$ appeared to be formed but attempts to effect separation by recrystallization method were unsuccessful. If $Mn(CO)_5OEt$ is being converted to $Mn_2(CO)_{10}$ this should not be CO-pressure dependent since the ratio of Mn to CO is the same in both compounds. If a mechanism involving the loss of two $\dot{O}Et$ radicals is envisaged then this <u>is</u> a CO-pressure dependent process:



$$2\ Mn(CO)_5OEt \xrightarrow{-2\dot{O}Et} Mn_2(CO)_{10} + \begin{array}{c} OEt \\ | \\ CO \\ | \\ OEt \end{array}$$

$Mn(CO)_5OEt$ has been successfully produced in a titanium autoclave, but the reactions in this study were undertaken in a stainless steel vessel. There may be some catalysis occurring from the Fe/$Fe(CO)_5$, or from traces of rhodium used in previous reactions. Using a glass insert in the autoclave may solve this problem.

B. Reactions of $Mn(CO)_5Br$ with Alcohols

(i) Ethane 1,2 diol

(1) $Mn(CO)_5Br$ (0.5g) was stirred with petroleum ether (10 ml, b.p. 100-120°C) and triethylamine (2 molar equivalents) and ethan-1,2-diol (2 molar equivalents) added. The mixture was then heated to 70°C for 1 hr. Toluene (5 ml) was added

to improve the miscibility of the reagents. Heating was continued at 70°C for a further 2hrs. with continuous stirring. The solution was cooled to room temperature and the solvent removed under vacuum. No new products were isolated.

IR (petroleum ether/toluene solution) ν(CO) 2045(w), 2030(w), 2010(w), 1940(s) cm^{-1}.

(2) IR (toluene solution, 5hrs. 70°C) ν(CO) 2045(m), 2030(m), 2010(m), 1940(s) cm^{-1}.

(3) IR (hexane solution, 2hrs. 70°C) ν(CO) 2045(m), 2020(s), 1980(w) cm^{-1}.

(4) IR (hexane solution, 5hrs. 50°C) ν(CO) 2045(m), 2020(s), 1980(w) cm^{-1}.

(ii) 2-chloroethanol

(5) $Mn(CO)_5Br$ (0.5g) was dissolved in toluene (5 ml) and triethylamine (2 molar equivalents) and 2-chloroethanol (2 molar equivalents) added. The solution was heated for 4 hrs. at 60°C with continuous stirring. The deep orange solution was cooled to room temperature and the solvent removed under vacuum. The residue was collected. Experimental data are collected in Table 3.1.

(6) 3 hrs. 60°C Orange solid isolated. Recrystallization was from H_2O (to remove $[NEt_3H]Br$) and CH_2Cl_2.

(7) Heated for 2 hrs. at 50°C. Orange solid isolated.

(8) Heated for 4 hrs. at 50°C. Bright yellow solid isolated.

(9) as (8).

(10) Heated for 6 hrs 50°C. Yellow-orange solid isolated. <u>TLC</u>: small samples of solid were dissolved in a little acetone and dichloromethane, spotted onto silica plates and toluene used to elute. The plates were then developed using iodine crystals. R_f values were measured.

(11) Heated for 6 hrs at 50°C. A further addition of NEt_3 and CH_2ClCH_2OH (1 molar equivalent) was made and heating continued for 3 hrs. at 50°C. A second addition was made and the solution heated for 2 hrs at 50°C. The toluene was removed under vacuum and the solid residue dissolved in dichloromethane before transferring to a separating funnel and washing with water to remove the $[NEt_3H]Br$. The dichloromethane was then removed under vacuum and an orange solid obtained. TLC as for (10).

(12) 1:4:4 molar ratios $Mn(CO)_5Br$: base : alcohol used initially and the solution heated to 50°C for 6 hrs. No indication of reaction and no new product isolated.

(13) As (12). Little sign of reaction, no new product isolated.

(14) 1:1:1 ratios $Mn(CO)_5Br$: base : alcohol used initially and the solution heated to 45°C for 3 hrs. 1:1 further addition of base and alcohol, and heating for further 1 hr. at 45°C. Insufficient product isolated to collect.

(15). 1:2:2 ratios reactants, heated for 3 hrs at 45°C and further addition (1:1) of base and alcohol made. Heating was continued for 1 hr. at 45°C. A dark orange solid was isolated.

(16) 1:2:2 ratios $Mn(CO)_5Br$: base : alcohol used initially, heated to 45°C for 3 hrs. A further addition of base and alcohol (1:1:1) was made and the solution heated for 5 hrs. at 60°C. Indication of reaction, but no new product was isolated.

(17) 1:2:2 ratios of reactants used initially and the solution heated at 45°C for 5 hrs. A further 1:1:1 addition of base and alcohol occurred and the solution heated for an hour at 45°C. A bright yellow solid was isolated.

(18) 1:1:1 ratio of reactants, heated for 5 hrs. at 45°C. A further 1:1:1 addition of base and alcohol was made with heating for 1 hr at 45°C. A dark yellow product was obtained in very low yield.

(iii) Water

(19) $Mn(CO)_5Br$ (0.5g) was dissolved in acetone (10 ml) and two molar equivalents of triethylamine added together with a large excess of water. The mixture was stirred at room temperature for 4 hrs. The solvent was then removed from the orange solution, the solid residue dissolved in dichloromethane and the solution transferred to a separating funnel to be washed with water to remove any $[NEt_3H]Br$. The dichloromethane was then removed to yield a bright yellow solid. Experimental data are collected in Table 3.2.

(20). As (19). Stirred for 7 hrs. at room temperature and then heated for 6 hrs. at 55°C. The yellow solid obtained was insufficient to be collected.

(21) Solution heated for 7 hrs at 40^{o}C, 3 hrs at 55^{o}C. A yellow solid was isolated.

(iv) ^{t} Butanol

(22) Mn(CO)$_5$Br (0.5g) was dissolved in toluene (15 ml) and two molar equivalents of triethylamine and ^{t}butanol added. The mixture was heated for 3 hrs at 50^{o}C and 7 hrs at 70^{o}C. The dark red-brown solution was cooled to room temperature, the solvent removed, and the solid residue dissolved in dichloromethane. The [NEt$_4$H]Br was extracted with water, and the solvent removed from the dichloromethane solution. A dark yellow-brown film was obtained which was insufficient for collection. Experimental data are collected in Table 3.3.

(23) Heated for 3 hrs 60^{o}C. A further addition of base and alcohol (1 molar equivalent) was made and the solution heated for a further 5 hrs at 60^{o}C. A third addition of base and alcohol was made and heating continued for a further 7 hrs at 70^{o}C. A fourth addition and 3 hrs heating at 70^{o}C followed. The pale yellow solution afforded no solid product.

(24) As (22) Heating for 6 hrs at 50^{o}C. A yellow-brown film was obtained from the dark brown solution, but it was not possible to isolate the small amount of product.

(25) As (22) with hexane as solvent. 9 hrs heating at 50^{o}C. The orange solution gave a yellow solid in small quantity.

(26) As (22) with toluene as solvent. 7 hrs heating at 45^{o}C and 7 hrs at 55^{o}C. A yellow-brown film only was obtained.

(27) As (22) with acetone as solvent. The mixture was heated for 11 hrs at 50°C. A further 2:1 molar equivalent of alcohol and base was added and heating continued at 50°C for 4 hrs. A deep orange solid was obtained.

(28) As (22). The solution was heated for 14 hrs at 50°C. A yellow-brown solid was obtained in a very small amount from the dark red-black solution.

C Phosphine Reactions : $Mn(CO)_4(PPh_3)Br$ with Alcohols

The apparent predominance of mixtures of alkoxide products and starting material lead to the idea of forming an intermediate $Mn(CO)_4LBr$ complex using L = PPh_3 which would then react completely to give $[Mn(CO)_2L(OR)]_n$

$$\begin{tikzcd}
Mn(CO)_5Br \arrow[r, "1\ \text{mole}\ PPh_3"] \arrow[d, "2\ \text{moles}\ PPH_3"'] & Mn(CO)_4LBr \arrow[d, "ROH"', "NEt_3"] \\
Mn(CO)_3L_2Br \arrow[r, "ROH/NEt_3"] & {[Mn(CO)_2L(OR)]_n} \\
{} \arrow[r, "''\quad ''"] & {[Mn(CO)L_2(OR)]_n}
\end{tikzcd}$$

Preparation of $Mn(CO)_4(PPh_3)Br$ (refs. [3],[4],[5]).

$Mn(CO)_5Br$ (0.5g) and PPh_3 (slightly in excess of 1 molar equivalent) were dissolved in toluene (20 ml) and the mixture heated for 2 hrs at 50°C.

IR (toluene solution) ν(CO) 2090(v.s.), 2010(v.s. broad), 1995(v.s., broad) 1950(vs,broad) cm^{-1}.

These figures match those of Atwood [5] for this complex.

Abel [4] found that the disubstituted produce $Mn(CO)_3L_2Br$ required heating to 120°C, and it was therefore assumed that the method used here does give the monosubstituted product only. The product was not isolated but used in further reaction.

$Mn(CO)_4(PPh_3)$ Br with Alcohols

(i) Ethanol

(29) Ethanol and triethylamine (1 molar equivalents) were added to the solution and the mixture heated for 1 hr at 50°C, 2 hrs 70°C and 2 hrs at 80°C. The solution was filtered and the solvent removed under vacuum . A bright yellow solid was obtained. Experimental data are collected in Table 3.4.

(30) As (29). Dark orange solution heated for 3 hrs at 70°C, and 2 hrs at 80°C. A further addition of base and alcohol (1 molar equivalent) was made after this time, and heating continued for 5 hrs at 80°C. A third addition of base and alcohol was made with heating continuing for 1 hr at 80°C. The solvent was removed and the solid residue washed with water. A dark yellow solid was isolated.

(31) As (29). Triethylamine and ethanol were added (3 molar equivalents) and the solution refluxed for 5 hrs at 100°C. The solvent was removed from the dark red-black solution and the residue washed with water. A light brown solid was isolated.

(32) As (29) Three molar equivalents of base and alcohol were added and the mixture heated to 100°C for 7 hrs. The same quantities of base and alcohol were then added after this heating period and heating continued at 100°C for 5 hrs. The solvent was removed, the solid residue dissolved in dichloromethane and this solution washed with water to remove the $[NEt_3H]Br$. The dichloromethane was removed to yield a bright yellow solid.

TLC Small samples of the compound were dissolved in acetone and dichloromethane, spotted onto silica plates and eluted with toluene. The plates were then developed with iodine crystals, and the R_f values measured.

(33) As (32). Three molar equivalents of triethylamine and ethanol were added and the mixture heated to 75°C for 6 hrs. A further three molar equivalents of base and alcohol were added with heating continuing at 75°C for another 6 hrs. A TLC as (32).

(ii) 2 Chloroethanol

(34) 2 chloroethanol and triethylamine (2 molar equivalents) were added and the solution heated for 3 hrs at 60°C and 7 hrs at 80°C. The solvent was removed under vacuum and the residue dissolved in dichloromethane. The solution was washed with water to remove $[NEt_3H]Br$ and the dichloromethane removed to yield a bright yellow solid. Experimental data are collected in Table 3.5.

(35) As (34) Base and alcohol (3 molar equivalents) were added initially with heating for 5 hrs at 80°C. Further addition of base and alcohol (1 molar equivalent) and heating for 7 hrs at 80^{o}C followed. A third addition of base and alcohol (1 molar equivalent) was made and heating continued for 3 hrs. No product was obtained from the pale yellow solution.

(36) As (34) Base and alcohol added as four molar equivalents and the solution heated for 19 hrs at 100^{o}C. From the pale yellow solution a cream coloured solid was isolated.

(iii) ^{t}Butanol

(37) As (34). Triethylamine and ^{t}butanol (two molar equivalents) were added to the phosphine complex solution and the mixture heated to 60^{o}C for 3 hrs and 80^{o}C for 7 hrs. A yellow-orange solid was obtained from the orange solution. Experimental data are collected in Table 3.6.

(38) As (37). Base and alcohol were added (3 molar equivalents) and the mixture refluxed at 100^{o}C for 5 hrs. A further molar equivalent of base and alcohol was added and the heating continued for an additional 9 hrs. A third addition of base and alcohol was made and the solution heated for a further 3 hrs. The yellow-orange solution yielded a bright yellow solid.

Section II

D Optimization of Reaction Conditions

In this section work carried out using alternative solvents and bases and chloropentacarbonylmanganese (I) in order to find the optimum conditions for yielding reliable and reproducible results is described.

Because manganese carbonyl halides are only sparingly soluble in hydrocarbon solvents but readily soluble in other organic solvents, acetone and alcohol were tried, the alcohol acting as both solvent and reactant. Acetone has a boiling point of 55°C and so is unsuitable for the phosphine reactions where toluene was retained as solvent.

Sodium carbonate and proton sponge were tried as bases in both sets of reactions, carbonate being of approximately the same basicity as triethylamine [6], but proton sponge is a very strong base and weak nucleophile due to steric effects [7].

Chloropentacarbonylmanganese (I) should be more reactive than the bromide to substitution of the halide by nucleophilic OR^- and a comparison of rate and conversion to products was made between the chloride and bromide. Experimental data are collected in Table 3.7.

(i) Acetone as Solvent

(39) $Mn(CO)_5Br/NEt_3/EtOH$

$Mn(CO)_5Br$ (0.5g) was dissolved in acetone (20 ml) and two molar equivalents of ethanol and triethylamine added. The solution as heated for 3 hrs at 45°C and then for 3 hrs at 50°C, a water-cooled reflux condenser being attached to the flask to prevent loss of solvent. A white precipitate was removed from the orange solution by filtration, and the filtrate reduced in volume to approx 3 ml before cooling it to -20°C. Solvent was then removed under vacuum to yield an orange solid.

(40) $Mn(CO)_5Br/NEt_3/CH_2ClCH_2OH$

As (39). The solution was heated for 3 hrs at 45°C and 3 hrs at 50°C. The dark red-brown solution yielded an orange-brown solid.

(ii) Ethanol as solvent

(41) $Mn(CO)_5Br$/Proton sponge

Two molar equivalents of proton sponge (1,8 bis (dimethylamino) napthalene) were added to $Mn(CO)_5Br$ (0.5g) dissolved in ethanol (20 ml). The mixture was heated for 10 hrs. at 50°C. The solvent was removed from the red/orange solution under vacuum and the solid residue dissolved in dichloromethane. This solution was transferred to a separating funnel and washed with water. The solvent was removed from the dichloromethane solution to yield a yellow solid which darkened to brown on standing.

(42) $Mn(CO)_5Br$/Sodium Carbonate

$Mn(CO)_5Br$ (0.5g) and a spatula measure of Na_2CO_3 were dissolved in ethanol (20 ml). The solution was heated for 10 hrs at 50°C before being filtered. The volume of the filtrate was reduced to 3 ml and cooled to -20°C. Solvent was then remove under vacuum to yield a yellow solid.

(iii) Base

(43) $Mn(CO)_5Br$/Proton Sponge/Ethanol

$Mn(CO)_5Br$ (0.5g) and two molar equivalents of proton sponge were dissolved in acetone (20 ml). The solution was heated for 2 hours at 45°C and for 7 hrs at 50°C and the dark orange solution filtered to remove the precipitated solid. The filtrate was reduced to 3 ml in volume and cooled to -20°C. Solvent was then removed under vacuum to yield a bright yellow solid.

(44) Mn(CO)$_5$Br/Sodium carbonate/Ethanol

Mn(CO)$_5$Br (0.5g) and Na_2CO_3 (spatula measure) were added to acetone (20 ml) and two molar equivalents of ethanol added. The mixture was heated for 8 hrs at 50°C, then filtered and reduced in volume as in (43). The dark red/black solution yielded dark red crystals.

(iv) Phosphine Complex Reactions with other bases

(45) Mn(CO)$_4$(PPh$_3$)Br/Proton Sponge/Ethanol

The phosphine intermediate Mn(CO)$_4$(PPh$_3$)Br was prepared as in the previous section. Two molar equivalents of proton sponge and ethanol were added to the toluene solution and the mixture heated for 15 hours at 70°C. The solvent was removed under vacuum from the yellow-orange solution. The residue was dissolved in dichloromethane and transferred to a separating funnel where it was washed with water. The dichloromethane was removed to yield an orange-brown solid.

(46) Mn(CO)$_4$(PPh$_3$) Br/Sodium carbonate/Ethanol

Two molar equivalents of ethanol and a spatula measure of sodium carbonate were added to the phosphine intermediate. The mixture was heated for 15 hrs. at 70°C, the yellow-orange solution filtered and reduced in volume to 3 ml before cooling to -20°C. Solvent was then removed to yield an orange-brown solid.

(47) $Mn(CO)_4(PPh_3)$ Br/Proton Sponge/Ethanol

Two molar equivalents of proton sponge and ethanol were added to the phosphine intermediate and the mixture heated to 100°C for 15 hrs. The solvent was removed from the red-orange solution and the solid residue dissolved in dichloromethane. The solution was transferred to a separating funnel and washed with water to remove the protonated base. The solvent was removed from the dichloromethane solution to yield a yellow-brown solid which becomes to pale brown on standing.

(48) $Mn(CO)_4(PPh)_3$ Br/Sodium carbonate/Ethanol

Two molar equivalent of ethanol and a spatula measure of sodium carbonate were added to the phosphine intermediate and the mixture heated for 16 hrs at 100°C. The orange solution was filtered and reduced to 3 ml in volume before cooling to -20°C. Solvent was then removed to yield a bright orange solid.

(v) $Mn(CO)_5Cl$ reactions

Preparation of $Mn(CO)_5Cl$

$Mn_2(CO)_{10}$ (6g) was dissolved in dichloromethane (80 ml). Chlorine was passed into the solution, via an oil bubbler and calcium chloride drying tower, which was kept at 0°C in an ice bath. Excess chlorine was dissolved in water. A steady flow of gas was maintained for 20 minutes during which time the $Mn(CO)_5Cl$ had precipitated as a pale yellow solid, together with some white $MnCl_2$. The volatile material was removed and the light-sensitive $Mn(CO)_5Cl$ purified by sublimation at 40°C (0.1 mm Hg).

(49) $Mn(CO)_5Cl$/Triethylamine/Ethanol

$Mn(CO)_5Cl$ (0.5g) was dissolved in acetone (20 ml) and two molar equivalents of triethylamine and ethanol added. a The mixture was heated for 10 hrs at 50°C. The solvent was removed from the orange solution and the solid residue dissolved in dichloromethane. This solution was transferred to a separating funnel and washed with water to remove $[NEt_3H]Br$. The dichloromethane was then removed under vacuum to yield a dark orange solid.

(50). $Mn(CO)_4(PPh_3)Cl$/Triethylamine/Ethanol

The phosphine intermediate was prepared as previously. Two molar equivalents of triethylamine and ethanol were added and the mixture heated to 70°C for 15 hrs. The toluene was removed from the orange-red solution and the solid residue treated as in (49). A bright yellow solid was obtained.

Section III

E. Further Reactions of $Mn(CO)_5Br$ with Alcohols

The reactions of $Mn(CO)_5Br$ with various alcohols was continued using sodium carbonate as the base and acetone as the solvent. Experimental data are collected in Table 3.8.

(i) Ethanol

(51) $Mn(CO)_5Br$ (0.5g) and a spatula measure of sodium carbonate were stirred with acetone (20 ml) and two molar equivalents of ethanol added. The mixture was heated at 45°C for 10 hrs before filtering the orange solution and reducing to 3 ml in volume. The solution was cooled to -20°C and the remaining solvent removed under vacuum to yield a bright orange solid.

(52). As (51). The mixture was heated for 18 hrs. at 50°C, 3 hrs. at 70°C and 7 hrs at 80°C. The red-brown solution yielded a yellow solid.

(ii) 2-Chloroethanol

(53) As (51). The mixture was heated for 9 hrs at 45°C. The orange solution gave a yellow solid which darkened to brown on standing.

(54) As (51). The mixture was heated for 12 hrs. at 50°C. The orange solution yielded a dark yellow solid.

(iii) Water

(55). As (51). A large excess of water was added, and the mixture heated for 9 hrs at 45°C. The orange solution yielded a dark yellow solid.

(56) as (51) the mixture was heated at 50°C for 12 hrs. The dark red-brown solution yielded a dark brown gelatinous solid.

(iv) ^{t}Butanol

(57). As (51). The mixture was heated for 9 hrs. at 45°C. The orange solution yielded a yellow solid which darkens to brown on standing.

(58). As (51). The mixture was heated for 12 hrs at 50°C. The orange solution yielded a bright yellow solid.

(v) Propan-2-ol

(59) As (51). The mixture was heated for 70 hrs. at 45°C. The orange solution yielded an orange solid.

(60). As (51). The mixture was heated for 30 hrs. at 50°C. The orange solution yielded a dark yellow solid.

(vi) Butan-1-ol

(61) As (51). The mixture was heated at 50°C for 20 hrs. The red-brown solution yielded a gelatinous solid of the same colour.

(vii) Triphenyl carbinol

(62) As (51). The mixture was heated for 11 hrs. at 50°C. The red-brown solution yielded a pale yellow solid.

(viii) 2-Methoxyethanol

(63). As (51). The mixture was heated for 12 hrs. at 50°C. The dark orange solution yielded a dark yellow solid.

(ix) Glycol

(64) As (51). The mixture was heated for 6 hrs. at 50°C. The dark orange/red solution yielded a dark yellow/brown solid.

(65) As (51). The mixture was heated for 4 hrs. at 50°C. The orange solution yielded a brown gelatinous solid.

(x) Acetoxime

(66). As (51). The mixture was heated for 4 hrs. at 50°C and the orange solution yielded a brown solid.

(xi) p-Nitrophenol

(67) As (51). The mixture was heated for 5 hrs. at 50°C and the orange solution yielded a solid of the same colour.

(xii) Benzyl Alcohol

(68). As (51) The solution as heated for 7 hrs at 50°C and the dark red/brown solution yielded a dark yellow/orange solid.

(xiii) 3-Buten-1-ol

(69) (as (51). The mixture was heated for 16 hours at 50°C and the orange solution yielded a dark orange solid.

(xiv) 2-Butyne-1,4-diol

(70) As (51). The mixture was heated for 5 hrs at 50°C and the dark orange solution yielded a yellow/orange solid in low yield.

(71) As (51). The mixture was heated for 9 hrs. at 50°C and the orange solution yielded a dark yellow/brown solid.

(xv) Ethanediol

(72) As (51). The mixture was heated for 14 hrs. at 50°C and the orange solution yielded a brown solid.

(xvi) Methanol

(73) As (51). The solution was heated for 10 hrs. at 50°C and the orange solution yielded a dark orange/brown solid.

F Further Phosphine Reactions: $Mn(CO)_4(PPh_3)Br$ with Alcohols

(i) Acetoxime

(74) The phosphine intermediate was obtained as previously. Two molar equivalents of acetoxime and a spatula measure of sodium carbonate were added to the phosphine intermediate in toluene solution (20 ml). The mixture was heated for 4 hrs. at 70°C before filtering the red/orange solution, reducing the volume to 3 ml and cooling to -20 C. The remaining solvent was removed under vacuum to yield a bright orange solid.

(75) As (74) The mixture was heated at 100°C for 4 hrs. and the dark red/black solution yielded a pale brown solid.

(76) As (74). Two molar equivalents of triethylamine and acetoxime were added to the phosphine intermediate in toluene solution. The mixture was heated for 10 hrs at 70°C and the dark red solution yielded a dark orange solid.

(77) As (76). The mixture was heated for 2 hrs. at 100°C and the dark red solution yielded an orange solid.

(78) As (76). The mixture was heated for 5 hrs. at 100°C and the bright orange solution yielded a solid of the same colour.

(ii) p-Nitrophenol

(79) As (74). The mixture was heated to 70°C for 19 hrs. and the yellow-orange solution yielded a dark yellow solid which becomes green on standing under nitrogen.

(80). As (79). The mixture was heated for 5 hrs. at 100°C, and the dark green solution yielded a solid of the same colour.

(81) As (79). The mixture was heated for 6 hrs. at 100°C and the dark red/orange solution yielded a dark yellow/green solid.

(iii) Triphenylcarbonol

(82) As (79). The mixture was heated at 70°C for 10 hrs. and the orange solution yielded a bright yellow solid.

(83). As (82) The mixture was heated for 11 hrs. at 100°C and the orange solution yielded a solid of the same colour.

(iv) Ethanediol

(84) As (79). The mixture was heated for 25 hrs. at 70°C, and the yellow/orange solution yielded a yellow solid.

(85) As (84). The mixture was heated for 17 hrs. at 100°C and the pale orange solution yielded a yellow solid.

G Purification of the Reaction Products

In the reactions described in sections B and C, two methods of purification of the products were used. Initially the solid obtained after removal of the solvent was washed with water to dissolve any [NEt_3H]Br and this solution filtered before drying the product and recrystallizing from toluene. This was not found to be generally suitable as the 2-chloroethanol reaction products seemed to be quite soluble in water.

The second method used was to dissolve the solid obtained from the reaction mixture in a small volume of dichloromethane (about 20 ml) and extract any [NEt_3]Br by repeated washing with small quantities of water (no more than 5 ml). This was repeated until the water washings showed no Br^- to be present when aqueous nitric acid and silver nitrate solutions were added dropwise. Although time consuming, this method does succeed in removing the [NEt_3H]Br from the product, which can then be recrystallized from toluene. Its major drawbacks are that some of the required product can be lost, and it is a method more suitable for carrying out in the laboratory atmosphere and so is not as suited to very air sensitive compounds. Fortunately the alkoxy derivatives obtained in this study appear to be much less air-sensitive than $Mn(CO)_5Br$.

With sodium carbonate as base the procedure was simply one of filtration (repeated if necessary) to remove the base and recrystallization of the collected product from toluene or dichloromethane.

After crystallization the products still contain starting material which has proved difficult to remove. One possible method was sublimation. Pure $Mn(CO)_5Br$ sublimes between 50 and 60°C at 0.1mmHg pressure. These conditions were tried with several samples but very little bromide was collected on the cold finger.

Another method tried was Soxhlet extraction. A small sample (0.1g) of the product from reaction (7) was placed on the sinter of the Soxhlet column and pentane (70 ml) heated to 60°C in the flask beneath. The extraction was run for a total of 13 hours (under a nitrogen atmosphere) before drying and collecting the solid residue. In theory the $Mn(CO)_5Br$ should be soluble to a greater extent in hot pentane whilst the products remain on the sinter. However, elemental analysis showed that starting material was still present and there was little difference in the percentage of bromine in the sample.

Attempts were then made to purify samples using fractional recrystallization techniques. Three samples were chosen to test the validity of these methods: (1) the product of reaction (50), a phosphine/ethanol reaction (2) the collected samples from the reactions of $Mn(CO)_5Br$ with ethanol (43,44,41,42,49,51,52), and (3) the collected samples from the reactions of $Mn(CO)_5Br$ with 2 chloroethanol (6,7,8,9,10,11,15,17,40,53,54). Each of the samples 1, 2 and 3 were dissolved in toluene, and the solvent partially removed slowly under vacuum. The solid which separated was dissolved in dichloromethane and the solvent reduced in volume as before. The solid produced was then submitted for C,H and N analysis.

Sample 1 gave a mixture of white and orange crystals which can be clearly seen with a hand lens. The sample was treated in this manner on three successive occasions and the results for carbon and hydrogen analysis are given below (no nitrogen was found) after each "purification":

C% = 65.40 H% = 4.05
70.16 4.54
62.06 5.16

average C% = 65.9

Possible products from the reaction are as follows, with toluene as occluded solvent:

$[Mn(CO)_2(PPh_3)(OEt)]_n$ C% = 63.16 H% = 4.78
$[Mn(CO)_2(PPh_3)(OEt)]_n.0.5C_6H_5CH_3$ 65.95 5.17
$[Mn(CO)_2(PPh_3)(OEt)]_n.1C_6H_5CH_3$ 68.24 5.4
$[Mn(CO)(PPh_3)_2(OEt)]_n$ 71.78 5.37

The most likely product is $[Mn(CO)_2(PPh_3)(OEt)]_n$ with some occluded toluene. The white crystals were thought to be triphenyl phosphine at first, but this seems unlikely in view of the high percentage carbon content found, 82.5%.

Sample 2 has had less work carried out on it, but the results of the purification after two repetitions of the procedure outlined above are:

C% = 31.32 H% = 3.08 N% = 3.68
24.84 1.99 0.67

The theoretical results for the expected product are:

$[Mn(CO)_3(OEt)]_n$ C% = 32.61 H% = 2.72

Sample 3 was purified as above but an interesting observation was made on adding the sample to water. A yellow solution was obtained which yielded a yellow solid on removing the water under vacuum. The analysis results for this solid together with the expected results are given below:

Sample 3, from water	C% =	32.06	H% =	1.98
$[Mn(CO)_3(OCH_2CH_2Cl)]_n$		27.46		1.83
$[Mn(CO)_3(OCH_2CH_2OH)]_n$		31.50		2.18

The latter compound would be obtained if reaction occurred with water, and if in the hydrolysis Cl^- was replaced by OH^-. It may be the case that removing the water under vacuum encourages loss of CO by the resultant reduction in vapour pressure and the product obtained may be polymeric.

A nujol mull of the yellow solid gave peaks in the IR spectrum > 2100 (w), 2050 (s), 2005 (w) cm^{-1}.

^1H spectra nmr were recorded in d_6-acetone for samples 1 and 3. Both spectra showed shifts in solvent signals of approximately 1 ppm due to the presence of some paramagnetic impurity. Assignable peaks for sample 1 are an intense singlet at 1.93 ppm (TMS), an intense singlet at 3.09 ppm (acetone), a weak singlet at 6.66 ppm (CH_2Cl_2), a weak singlet at 8.22 ppm ($CHCl_3$), and a weak singlet at 8.51 ppm and a weak multiplet at 8.85 ppm (PPh_3). Peaks assigned to the complex are a broad multiplet at 3.97 ppm and a weak singlet at 4.34 ppm.

Sample 3 showed an intense solvent peak at 3.20 ppm and a weaker singlet at 8.33 ppm ($CHCl_3$) and some very weak multiplets at 5.4 and 5.5 ppm which were assigned to the complex.

The peak broadening could be due to the presence of paramagnetic material, exchange with acetone or fluxionality of the molecule.

Further work needs to be carried out to purify all the compounds prepared, but it may prove necessary to use fractional crystallization or chromatography on basic alumina (cf. Abel [2]) in order to separate, the products from starting material.

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Table 3.I Experimental Data for Reactions of $Mn(CO)_5Br$ with 2-Chloroethanol

Reaction Number	IR ν(CO) cm^{-1} Toluene Solution	Analytical Data %	Mass Spectrum: Highest m/e value (CI)	Additional Data
5	2I40(w), 2040(s), 2020(sh), I990(w), I930(s, broad)			
6	2080(m), 2040(m), 2030(s), 20I0(s), I985(w), I925(s, broad)	C 29.06, H 5.93, N 0.95, Mn II.9I		^1H nmr, $CDCl_3$ solution, 25°C, intense singlet -0.0078 ppm (TMS); singlet 7.26 ppm ($CHCl_3$); singlet I.25 ppm common to (6) & (7)
7	2080(m), 2030(s), 20I0(s), I990(sh), I9I0(s, broad)	C 30.64, H 5.29, N 0.70, Mn I2.37	759, trimer or higher oligomer fragment. Further CO loss observed at high mass, but a fragmentation pattern cannot be deduced.	^1H nmr, $CDCl_3$ solution 25°C, intense singlet 0.03I ppm (TMS), singlet 7.26 ppm ($CHCl_3$), singlet I.25 ppm common to (6) & (7)
8	2035(sh), 2005(s), I980(sh), I900(s, broad)	C 30.86, H 5.49, N I.84, Mn I2.06	480, trimer or higher oligomer fragment. Sequential loss of 8CO's. Relatively intense peaks at m/e=I73, I30, I03 and 86	
9	2080(w), 2040(w), 20I0(s), I985(w), I9I5(s, broad)	C 29.07, H 5.35, N 2.44, Mn I2.74	725, requiring at least a trimeric complex. Relatively intense peaks at m/e=672, 598, 524 and 435 $[Mn_2(CO)_6(OR)_2{}^+]$	
I0	2030(s), 20I0(s), I9I0(s, broad)	C 24.89, H 2.84, N 0.I2, Mn 23.0, Br 9.06	I094; $[Mn(CO)_5(OR)^+]$, M_r=I092.5 Some fragmentation by CO loss at high mass. Relatively intense peaks at m/e=362, 208, I44, I30, II6, I08, I02, 86, 44	TLC: R_f(acetone) = 0.23 and 0.67 R_f(CH_2Cl_2) = 0.48 and 0.73; 0.34 and 0.65 (2 plates)

II	2050(m),2040(s), 2020(m),I980(v.w.) I940(s,broad)	C 30.75, H 2.92, Mn 22.92, Br I0.5I	833, requiring at least a pentameric complex. Relatively intense peaks found at m/e=279,I30,I08, I02,6I. No clear fragmentation pattern.	TLC: R_f(acetone)= 0.28 and 0.74 $R_f(CH_2Cl_2)$=0.48 and 0.74; 0.38 and 0.72 (2 plates)
I2	2050(s),2020(s, broad),I980(m), I930(s,broad)			
I3	2050(s),2020(s, broad),20I0(s, broad),I980(m), I930(s,broad)			
I4	2080(w),2030(s), 20I0(s),I920(s, broad)			
I5	2080(w),2030(s), 20I0(s),I905(s, broad)	C 26.48, H 3.66, N 0.2I, Mn 22.36, Br 7.I4	603. Trimer or higher oligomer fragment. No discernible fragmentation pattern.	
I6	2040(m),2030(s), 20I0(s),I985(m), I920(s,broad)			
I7	2030(s),20I0(s), I940(s,broad), I920(sh)	C 24.74, H 3.38, Mn 20.60, Br 8.50	I370, requiring at least a heptameric complex. Relatively intense peaks at m/e = 252,223, but no discernible fragmentation pattern as peaks of low intensity.	

I8	2080(w),2035(w), 20I0(s),I920(s, broad)	$[Mn(CO)_4(OCH_2CH_2Cl)]_2$ requires C 29.2I, H I.62, Mn 22.3I $[Mn(CO)_3(OCH_2CH_2Cl)]_n$ requires C 27.46, H I.83, Mn 25.I7

Table 3.2 Experimental Data for Reactions of $Mn(CO)_5Br$ with Water

Reaction Number	IR ν(CO) cm^{-1} Acetone Solution	Analytical Data %	Mass Spectrum: Highest m/e value (CI)
I9	2030(s),20I0(sh),I965(s), I920(s,broad)	C 24.9I, H 2.9I, N 0.44, Mn 25.I2, Br 3.78	309, requiring at least a trimeric complex. Relatively intense peaks found at m/e = 380,I95,57,43,39,27 No obvious fragmentation pattern.
20	At room temp. as (I9) After heating: 2030(s), I9I5(s,broad)		
2I	2020(s),I9I5(s,broad)	C 24.68, H 2.37, N 0.I3, Mn 28.2I, Br 2.59	592, requiring at least a tetrameric complex. Relatively intense peaks found at m/e = I02,86,60. No discernible fragmentation pattern, peaks of low intensity.
		$Mn(CO)_5OH$ requires C 28.30, H 0.47, Mn 25.94 $[Mn(CO)_4OH]_2$ requires C 25.09, H 0.54, Mn 29.89 $[Mn(CO)_3OH]_n$ requires C 23.07, H 0.64, Mn 35.26	

Table 3.3 Experimental Data for Reactions of $Mn(CO)_5Br$ with $^tButanol$

Reaction Number	IR ν(CO) cm^{-1} Toluene solution unless stated	Analytical Data %	Mass Spectrum: Highest m/e value (CI)
22	2080(m),2045(s),20I5(s), I985(s),I940(s,broad)		
23	2050(s),2020(s),I980(w), I945(s)		
24	2045(s),2030(sh),20I0 (v.s.),I978(m),I938(m)		
25	Hexane 2050(v.s.),20I0(s), 2000(s),I980(w),I950(w)		
26	2085(w),2040(s),2025(sh), 20I0(v.s.),I985(w),I940(s)		
27	Acetone 2025(s),20I0(m),I970(m, broad),I925(s,broad), I900(sh)	C 27.43, H 2.82, Mn 20.55, Br 4.28	II55/683 (2 spectra) 683: tetrameric or higher oligomeric fragment. Relatively intense peaks at m/e = 2I2 $[Mn(CO)_3(OBu^t)^+]$, I70, I30, I02, 89 II55: hexameric or higher oligomeric fragment. Cleavage into trimers is seen, together with initial CO and OR loss.
28	2080(m),2050(s),20I0(s), I985(s), I940(s)		
		$[Mn(CO)_4(OBu^t)]_2$ requires C 40.00, H 3.75, Mn 22.92 $[Mn(CO)_3(OBu^t)]_n$ rquires C 39.62, H 4.25, Mn 25.94	

Table 3.4 Experimental Data for Reactions of $Mn(CO)_4(PPh_3)Br$ with Ethanol

Reaction Number & Temp.	IR ν(CO) cm^{-1} Toluene solution	Analytical Data %	Mass Spectrum: Highest m/e value (CI)	Additional Data
29 (80°C)	2085(m),20I0(sh), 2005(sh),I990(s), I950(s)	C 47.60, H 4.74, N I.4I, Mn 8.67	447, $[Mn(CO)_3L(OR)^+]$ i.e. dimer cleaved in spectrometer. Relatively intense peak at m/e = 262(PPh_3^+)	
30 (80°C)	2080(m),2020(sh), 20I0(w),I990(s), I950(s,broad)	C 53.84, H 4.23, Mn I0.00, Br 6.38	706, requiring at least a dimeric complex. Relatively intense peaks found at m/e= 447,262(PPh_3),I02,74	^{1}H NMR, $CDCl_3$ soln., 25°C; intense singlet 0.00ppm(TMS) singlet 7.26ppm($CHCl_3$) singlets 7.38,7.46, 7.63 and 7.75ppm (PPh_3), singlet I.57 ppm.
3I (I00°C)	I943(s),I9I5(s)	C 65.29, H 5.23, Mn 7.90, Br I.90	837, dimeric or higher oligomeric fragment. Relatively intense peaks found at m/e = 262(PPh_3),I83,I03,5I	^{1}H NMR, $CDCl_3$ soln., 25°C; intense singlet 0.00I3ppm (TMS), singlet 7.26 ppm($CHCl_3$), singlet 7.33ppm and multiplet 7.55ppm (PPh_3), singlet I.57ppm.
32 (I00°C)	2060(w),I995(s), I9I5(s)	C 70.I8, H 5.33, N 0.20, Mn 3.28	II96, fragment of trimer or higher oligomer. Peak found at m/e = 838 half a tetrameric complex, but peak is weak in intensity. Relatively intense peak at m/e = 447 $[Mn(CO)_3(PPh_3)OEt^+]$	^{1}H NMR, $CDCl_3$ soln., 25°C; intense singlet -0.00Ippm (TMS), singlet 7.26ppm, ($CHCl_3$), doublets 7.33 and 7.39ppm and two doublets centred at 7.54 and7.75ppm (PPh_3), singlet I.57 ppm.

				TLC: R_f(acetone)=0.57 and 0.88. R_f(CH_2Cl_2)=0.86 and 0.84 (2 plates)
33 (75°C)	2085(m),20I0(sh), 2005(s),I945(s)	C 60.05, H 4.52, Mn 6.37, Br I.28	II03, trimer or higher oligomer fragment. Peak at m/e=448 is as intense as the base peak and corr-esponds to $[Mn(CO)_4(PPh_3)(OEt)^+]$ Other relatively intense peaks at m/e=59I,579,525	^{1}H NMR, $CDCl_3$ soln., 25°C; intense singlet 0.00ppm (TMS) singlet 7.26ppm($CHCl_3$) Two singlets 7.38 and 7.46ppm and a multi-plet centred at 7.75 ppm(PPh_3), singlet I.57 ppm. TLC: R_f(CH_2Cl_2)=0.48 and 0.8I; 0.42 and 0.85 (2 plates)
		$[Mn(CO)_2(PPh_3)_2(OEt)]_2$ requires C 70.59, H 5.I5, Mn 8.09 $[Mn(CO)_3(PPh_3)OEt]_2$ requires C 6I.88, H 4.48, Mn I2.33 $[Mn(CO)_2(PPh_3)OEt]_n$ requires C 63.I5, H 4.78, Mn I3.I5		

Table 3.5 Experimental Data for Reactions of $Mn(CO)_4(PPh_3)Br$ with 2-Chloroethanol

Reaction number (Reaction Temp.)	IR ν(CO) cm^{-1} Toluene solution	Analytical Data %	Mass Spectrum: Highest m/e value(CI)
34 (80°C)	2080(m),20I0(sh),2000 (sh), I990(m),I950(s, broad)	C 6I.40, H 5.07, Mn 4.I0, Br 6.40	808, dimeric or higher oligomeric fragment. Relatively intense peaks found at m/e = 445,4I9,369, 3I8, $[Mn(CO)_2PPh_3^+]$ and 262 (PPh_3^+)
35 (80°C)	I990(w),I945(s),I9I8(w)		
36 (I00°C)	I990(w),I945(s),I9I8(w)	C 60.49, H 6.89, Mn 0.I8, Br 0.84	633, requiring at least a dimeric complex. Relatively intense peaks at m/e = 463,447,445
		$[Mn(CO)_3(PPh_3)(OCH_2CH_2Cl)]_2$ requires C 57.44, H 3.95, Mn II.45 $[Mn(CO)_2(PPh_3)(OCH_2CH_2Cl]_n$ requires C 58.34, H 4.20, Mn I2.I5	

Table 3.6 Experimental Data for Reactions of $Mn(CO)_4(PPh_3)Br$ with ᵗButanol

Reaction number (Reaction Temp.)	IR ν(CO) cm^{-1} Toluene solution	Analytical Data %	Mass Spectrum: Highest m/e value(CI)
37 (80°C)	2080(w),2000(w),I990(s), I953(s)	C 57.42, H 4.48, Mn 6.70, Br 8.90	764 $[Mn_2(CO)_2(PPh_3)_2(OR)^+]$ Relatively intense peaks at m/e =580,445 $[Mn(CO)_2PPh_3(OR)^+]$ or $[Mn_2(PPh_3)(OR)^+]$,369, $[Mn(CO)_4(PPh_3)^+]$,262(PPh_3^+)
38 (I00°C)	2065(w),I946(s),I9I8(s)	C 66.23, H 5.79, Mn 2.80, Br I.59	EI 857, $[Mn_2(CO)_2(PPh_3)_2^+]$ Relatively intense peaks at m/e = 557,479,463,445, $[Mn(CO)_2PPh_3(OR)^+]$
		$[Mn(CO)_3(PPh_3)(OBu^t)]_2$ requires C 63.29, H 5.06, Mn II.60, $[Mn(CO)_2(PPh_3)(OBu^t)]_n$ requires C 64.57, H 5.38, Mn I2.33	

Table 3.7 Experimental Data for Reactions in the Optimization Studies

Reaction Number	Conditions Solvent/Base/ Alcohol	IR ν(CO) cm^{-1}	Analytical Data %	Mass Spectrum: Highest m/e value(CI)
39	Acetone NEt_3 Ethanol	2020(s),20I0(sh), I973(w),I9I5(s, broad)	C 30.59, H 4.I6, N 2.I3, Mn 24.3I, Br I4.40 $[Mn(CO)_4(OEt)_2]$ requires C 33.96, H 2.36, Mn 25.94 $[Mn(CO)_3(OEt)]_n$ requires C 32.6I, H 2.I7, Mn 29.89	
40	Acetone NEt_3 2-Chloro-ethanol	2025(s),20I0(sh), I975(w),I9I8(s)	C 2I.07, H 3.45, N I.95, Mn 26.52, Br 22.77 $[Mn(CO)_4(OCH_2CH_2Cl)]_2$ requires C 29.2I, H I.62, Mn 22.3I $[Mn(CO)_3(OCH_2CH_2Cl]_n$ requires C 27.46, H I.83, Mn 25.I7	
4I	Ethanol Proton Sponge Ethanol	2020(s),20I0(m), I990(s),I920(s), I890(s)	C II.20, H 2.32, Mn I6.95, Br 35.40 Required: as (39)	538/906 (2 spectra), fragments of a trimer or higher oligomer. Relatively intense peaks found at m/e=447,2I5,49 (538 spectrum) and 447,2I3 $(Mn(CO)_4(OR)^+)$ I36 (906 spectrum)
42	Ethanol Na_2CO_3 Ethanol	2030(m),20I0(w), 2000(sh),I998(s), I920(sh),I895 (v.s.)	C 56.54, H 6.I2, Mn II.II, Br 2.62 Required: as (39)	447, requiring at least a trimeric complex. Relatively intense peak at m/e=2I3$(Mn(CO)_4(OEt)^+)$

43	Acetone Proton Sponge Ethanol	20I0(s),I972(s), I935(s)	C 32.57, H 3.43, N 3.48, Mn I5.43, Br 22.43 Required: as (39)	584, requiring at least a tetrameric complex. Relatively intense peaks found at m/e=447,2I5 ($Mn(CO)_4(OEt)^+$ M_r=2I2), I84 ($Mn(CO)_3(OEt)^+$)
44	Acetone Na_2CO_3 Ethanol	2030(s),20I0(sh), I972(w),I920(s)	C 40.3I, H 5.I2, Mn 27.I9, Br 8.26 Required: as (39)	464, requiring at least a trimeric complex. Relatively intense peaks found at m/e=447,I34,99,76
45	PHOSPHINE 70°C Toluene Proton Sponge Ethanol	2090(w),2060(w), 20I0(w),I990(w), I952(s)	C 68.76, H 6.67, N 5.34, Mn 2.27, Br 2.03 $[Mn(CO)_3(PPh_3)(OEt)]_2$ requires C 6I.88, H 4.48, Mn I2.33; $[Mn(CO)_2(PPh_3)_2(OEt)]_2$ requires C 70.59, H 5.I5, Mn 8.09; $[Mn(CO)_2(PPh_3)(OEt)]_n$ requires C 63.I5, H 4.78, Mn I3.I5	354, requiring at least a dimeric complex. A relatively intense peak was found at m/e=2I4 ($Mn(CO)_4OEt^+$ or proton sponge)
46	PHOSPHINE 70°C Toluene Na_2CO_3 Ethanol	2085(w),2025(m), 2000(w),I990(m), I950(s),I9I5(s)	C 60.27, H 5.20, Mn 6.74, Br 2.27 Required: as (45)	970, requiring at least a trimeric complex. A relatively intense peak was found at m/e=262 (PPh_3^+)
47	PHOSPHINE I00°C Toluene Proton Sponge Ethanol	2060(w),I980(sh), I955(s),I9I5(s)	C 72.93, H 6.94, N 5.II, Mn 2.79, Br 0.84 Required: as (45)	637, corresponding to a fragment of a dimer or higher oligomeric complex. Relatively intense peaks were found at m/e=564,476,307,290

48	PHOSPHINE I00°C Toluene Na_2CO_3 Ethanol	2040(w),I980(sh), I955(s,broad)	C 67.33, H 5.33, Mn 4.33, Br 0.89 Required: as (45)	577, $(Mn(PPh_3)_2^+)$. Relatively intense peaks found at m/e=278,262 (PPh_3^+)
49	$Mn(CO)_5Cl$ Acetone NEt_3 Ethanol	2030(v.s.),I990 (sh),I978(sh),I970 (w),I920(v.s., broad),I863(m)	C 27.I2, H 3.39, Mn 23.2I, Cl 0.53 Required: as (39)	757, requiring at least a pentameric complex. Relatively intense peaks were found at m/e=I82 $(Mn(CO)_3OEt^+)$,I02
50	$Mn(CO)_4(PPh_3)$ Cl 70°C Toluene NEt_3 Ethanol	2085(m),2050(w), 20I0(m),I990(s), I950(s,broad)	C 68.28, H 4.8I, Mn 6.33, Cl 2.69 Required: as (45)	EI 464, requiring at least a dimer. Relatively intense peak at m/e = 262 (PPh_3^+)

Table 3.8 Experimental Data for Further Reactions of $Mn(CO)_5Br$ with Alcohols

Reaction Number	Alcohol	IR ν(CO) cm⁻¹	Analytical Data %	Mass Spectrum: Highest m/e value(CI)
5I	Ethanol	2038(s),20I8(s), I978(s),I930(s, broad)	C I8.65, H0.89, Mn 20.I4, Br 26.35 $[Mn(CO)_4(OEt)]_2$ requires C 33.96, H 2.36, Mn 25.94, $[Mn(CO)_3(OEt)]_n$ requires C 32.6I, H 2.I7, Mn 29.89	987, requiring at least a hexameric complex, $Mn_6(CO)_{17}(OEt)_4$ fragment. Relatively intense peak found at m/e = I83, $Mn(CO)_3(OEt)^+$
52	"	2022(s),I9I5(s, broad)	C I8.09, H 3.52, Mn 2I.79, Br I7.62 Required: as (5I)	II05, requiring at least a hexameric complex. Relatively intense peaks found at m/e=I84($Mn(CO)_3OEt^+$),II6,I02,99,76. The parent ion appears to fragment slowly by loss of CO and OEt
53	2-Chloro-ethanol	2030(s),20I0(w), I995(sh),I925(s, broad)	C I8.7I, H 2.34, Mn 32.38, Br I2.2I $[Mn(CO)_4(OCH_2CH_2Cl)]_2$ requires C 29.2I, H I.62, Mn 22.3I $[Mn(CO)_3(OCH_2CH_2Cl)]_2$ requires C 37.46, H I.83, Mn 25.I7	446, requiring at least a dimer. Possibly a tetramer fragment ($Mn_4(CO)_8{}^+$)
54	"	2035,(s),20I0(sh), 2000(sh),I925(s, broad)	C 2I.I7, H I.42, Mn 29.85, Br I2.39 Required: as (53)	278, requiring at least a dimer. Possibly trimer ($Mn_3(CO)_4{}^+$) or tetramer ($Mn_4(CO)_2{}^+$) fragments.
55	Water	2030(v.s.),20I0 (sh),I975(w),I920 (v.s.,broad),I860 (s)	C I3.65, H 0.83, Mn 24.03, Br 25.42 $[Mn(CO)_4(OH)]_2$ requires C 26.09, H 0.54, Mn 29.89 $[Mn(CO)_3OH]_n$ requires C 23.07, H 0.64, Mn 35.26	424, requiring at least a trimeric complex ($Mn_3(CO)_8(OH)_2{}^+$ fragment). Some CO loss is evident (non-sequential)

56	"	2035(v.s.),I980(w), I925(v.s.,broad)	C 39.23, H 4.49 Required: as (55)	
57	^{t}Butanol	2030(v.s.),I920 (v.s.,broad)	C 22.67, H 2.30, Mn 3I.42, Br I4.I7 $[Mn(CO)_4(OBu^t)]_2$ requires C 40.00, H 3.75, Mn 22.92 $[Mn(CO)_3(OBu^t)]_n$ requires C 39.62, H 4.25, Mn 25.94	834, requiring at least a tetramer
58	"	2030(v.s.),I923 (v.s.)	C 22.94, H I.46, Mn 30.2I, Br 6.49 Required: as (57)	EI 503, requiring at least a trimer. Possibly a tetramer fragment $(Mn_4(CO)_{10}^+]$ Relatively intense peak found at m/e 207
59	Propan-2-ol	2030(v.s.),20I0 (w),I972(m),I920 (v.s.,broad)	C 23.64, H I.95, Mn 30.2I, Br 7.28 $[Mn(CO)_4(OCH(CH_3)_2)]_2$ requires C 37.I7, H 3.I0, Mn 24.34 $[Mn(CO)_3(OCH(CH_3)_2)]_n$ requires C 36.36, H 3.54, Mn 27.78	609, requiring at least a tetrameric complex. A relatively intense peak was found at I02, but no obvious fragmentation pattern was evident.
60	"	2020(v.s.),I905 (v.s.,broad)	C I8.03, H 2.32, Mn 27.7I, Br I3.00 Required: as (59)	535, requiring at least a trimeric complex, $[Mn_3(CO)_4(OR)_2^+]$ fragment. Relatively intense peaks are found at m/e=392 $[Mn_2(CO)_8(OR)^+]$,279,$[Mn_2(CO)_6^+]$ I83,I02
6I	Butan-I-ol		C 48.05, H 6.28, $[Mn(CO)_4(O(CH_2)_3CH_3]_2$ requires C 40.00, H 3.75, Mn 22.92 $[Mn(CO)_3(O(CH_2)_3CH_3)]_n$ requires C 39.62, H 4.24, Mn 25.94	

62	Triphenyl-carbinol	2030(sh),20I0(s), I975(s),I925(v.s. broad)	C 74.9I, H 4.I3, Mn 7.04, Br 8.36 $[Mn(CO)_4(OCPh_3)]_2$ requires C 64.78, H 3.52, Mn I2.9I $Mn(CO)_5(OCPh_3)$ requires C 63.44, H 3.30, Mn I2.II	4I0, requiring a monomeric complex or higher oligomer. Relatively intense peaks found at m/e =260(OR^+), 243 $[Mn(CO)_3(OCPh)^+]$
63	2-Methoxy-ethanol	2040(sh),2030(s), 20I0(s),I9I5(v.s., broad)	C 22.75, H I.8I, Mn 25.40, Br 4.67 $[Mn(CO)_4(OCH_2CH_2OCH_3)]_2$ requires C 34.7I, H 2.89, Mn 22.73 $[Mn(CO)_3(OCH_2CH_2OCH_3)]_n$ requires C 33.64, H 3.27, Mn 25.70	833, requiring at least a tetrameric complex. Relatively intense peaks found at m/e=390,278,262,22I,94. No obvious fragmentation pattern is evident.
64	Glycerol	2030(m),20I0(v.s.) I900(v.s.)	C 22.02, H 3.I9, Mn 23.97, Br 7.47 $[Mn(CO)_4(OCH_2CHOHCH_2OH)]_2$ requires C 32.56, H 2.7I, Mn 2I.32 $[Mn(CO)_3(OCH_2CHOHCH_2OH)]_n$ requires C 3I.30, H 3.04, Mn 23.9I	535, requiring at least a trimeric complex with alkoxide ion bound by only one oxygen atom. Relatively intense peaks found at m/e=296,279,263,I66. No obvious fragmentation pattern is evident
65	"	2030(m),20I0(v.s.) I900(v.s.)		
66	Acetoxime	2025(v.s.),I9I5 (v.s.,broad)	C 27.79, H 2.74, N 4.64, Mn 23.80, Br 8.68 $[Mn(CO)_4(ON{=}CMe_2)]_2$ requires C 30.I2, H 2.5I, N 5.86, Mn 23.0I $[Mn(CO)_3(ON{=}CMe_2)]_n$ requires C 34.I2, H 2.84, N 6.64, Mn 26.07	335, requiring at least a dimeric complex. Possibly a trimer $[Mn_3(CO)_6{}^+]$ or tetramer $[Mn_4(CO)_4{}^+]$ fragment. Relatively intense peaks were found at m/e =263,58

67	p-Nitrophenol	2030(v.s.),20I0 (sh),2000(sh), I925(v.s.,broad)	C 4I.82, H I.90, N 5.97, Mn I0.78, Br I.05 $[Mn(CO)_4(OC_6H_4NO_2)]_2$ requires C 39.34, H I.3I, N 4.59, Mn I8.03 $[Mn(CO)_3(OC_6H_4NO_2)]_n$ requires C 38.99, H I.44, N 5.05, Mn I9.86	6I6, requiring at least a trimeric complex. A large number of relatively intense peaks were found, including m/e=488,447,354,3I5,285,278($Mn(CO)_3OR^+$) 269,257,24I,2I3,204,I39(OR^+)
68	Benzyl Alcohol	2030(v.s.),20I0 (sh),I990(w),I980 (v.w.),I925(v.s., broad)	C 32.92, H 2.37, Mn 24.35, Br 2.7I $[Mn(CO)_4(OCH_2Ph)]_2$ requires C 48.I8, H 2.I9, Mn 20.07 $[Mn(CO)_3(OCH_2Ph)]_n$ requires C 48.78, H 2.85, Mn 22.36	590, requiring at least a trimeric complex. Possibly a tetrameric fragment $[Mn_4(CO)_{12}(OCH_2)^+]$. Relatively intense peaks found at m/e=246($Mn(CO)_3(OR)^+$), I97,I8I,I69,II9,I07(OR^+),92,79
69	3-Buten-I-01	2030(s),20I0(s), I975(m),I925(s, broad)	C I8.87, H I.26, Mn I8.68, Br 23.80 $[Mn(CO)_3(OCH_2CH_2CH{=}CH_2)]_n$ requires C 40.00, H 3.33, Mn 26.I9	576, requiring at least a trimeric complex. A relatively intense peak was found at m/e=447 $[(Mn(CO)_3(OR))_2^+]$ No obvious fragmentation pattern.
70	2-Butyne-I,4-diol	2040(s),2020(s), 2005(sh),I905 (v.s.,broad)		
7I	"	2040(s),2020(s), 2005(sh), I905 (v.s.,broad)	C 33.58, H 3.I8, Mn I9.7I Br 3.20 $[Mn(CO)_2(OCH_2C{\equiv}C.CH_2O)]_n$ requires C 36.92, H 2.05, Mn 28.2I	466, requiring at least a trimeric complex. No obvious fragmentation pattern.

72	Ethanediol	2040(w),2030(v.s.), 20I0(v.s.),I960(s), I905(v.s.,broad)	C 22.26, H 2.49, Mn 23.94, Br 7.52 $[Mn(CO)_3(OCH_2CH_2OH)]_n$ requires C 30.00, H 2.50, Mn 27.50	I058, requiring at least a hexameric complex. No obvious fragmentation pattern.
73	Methanol	2035(v.s.),20I0(sh), I930(v.s.,broad)	C I9.7I, H I2.75, Mn 3I.43, Br 5.03 $[Mn(CO)_3(OMe)]_n$ requires C 28.23, H I.76, Mn 32.35	685, (780 EI), requiring at least a pentameric complex. No obvious fragmentation pattern.

Table 3.9 Experimental Data for Further Reactions of $Mn(CO)_4(PPh_3)Br$ with Alcohols

Reaction Number	Alcohol	Conditions Solvent/Base Temp.(°C)	IR ν(CO) cm^{-1}	Analytical Data %	Mass Spectrum: Highest m/e value (CI)
74	Acetoxime	Toluene Na_2CO_3 70	2090(m),2075(s), 20I0(m),I945(s, broad),I922(w), I908(m)	C 59.44, H 4.44, Mn 6.25, Br 5.74 $[Mn(CO)_3(PPh_3)(ON=CMe_2)]_2$ requires C 60.88, H 4.44, Mn II.63, N 2.96 $[Mn(CO)_2(PPh_3)_2(ON=CMe_2)]_2$ requires C 64.72, H 4.72, Mn II.23, N 3.I5	523. Relatively intense peaks found at m/e=447,263(PPh_3^+). No obvious fragmentation pattern. No N thus fragments of a Mn/CO/PPh /Br complex
75	"	Toluene Na_2CO_3 I00	2000(w),I990(w), I940(m)	C 63.34, H 5.57, Mn 2.58, Br 3.46 Required: as(74)	557. Relatively intense peaks found at m/e=279,263(PPh_3^+). Fragments of Mn/CO/PPh /Br complex as no N. No fragmentation pattern evident.
76	"	Toluene NEt_3 70	2025(v.s.),2005 (sh),I935(s), I920(sh),I905(s)	C 62.I8, H 4.92, N I.66, Mn 8.I9, Br 4.00 Required: as (74)	558, requiring at least a dimeric complex. Possibly a $(Mn_2(CO)_4(PPh_3)OR^+)$ fragment. Relatively intense peaks found at m/e=305, 263(PPh_3^+),I85
77	"	Toluene NEt_3 I00	2080(w),2020(v. s.),20I0(w),I935 (s),I905(s)	C 64.50, H 4.75, N I.58, Mn 7.43, Br I.24 Required: as (74)	555, requiring at least a dimeric complex. Possibly a $(Mn_2(CO)_4(PPh_3)OR^+)$ fragment. Relatively intense peaks found at m/e=447 $(Mn(CO)_2(PPh_3)(OR)^+)$,370,305,262 (PPh_3^+)
78	"	Toluene NEt_3 I00	2020(w),I990(w), I94I(s),I925(m)	C 77.59, H 5.69, N 0.38, Mn 3.2I, Br 0.68 Required: as(74)	89I, requiring at least a dimeric complex. Possibly a $(Mn_2(CO)_4(PPh_3)_2(OR)_2^+)$ fragment. A relatively intense peak was found at m/e=262(PPh_3^+)

79	p-Nitro-phenol	Toluene NEt_3 70	2090(m),2025(w), 20I0(s),I950(s, broad)	C 49.44, H 5.00, N I.52, Mn 5.44, Br 8.28 $[Mn(CO)_4(PPh_3)(OC_6H_4NO_2)]$ requires C 59.26, H 3.35, N 2.42, Mn 9.70	502, requiring a monomer or higher oligomeric complex. Relatively intense peaks found at 305 ($Mn(CO)_4(OR)^+$),263(PPh_3^+) I40($Mn(CO)_3^+$)
80	"	Toluene NEt_3 I00	2I60(w),I990(w), I947(s,broad)	C 65.59, H 5.07, N I.I3, Mn I.33, Br 2.26 Required: as (79)	554, requiring a monomer or higher oligomer. Relatively intense peaks found at m/e = 447,262(PPh_3^+).No obvious fragmentation pattern.
8I	"	Toluene NEt_3 I00	2080(m),2020(sh), 2000(m),I945(s, broad)	C 72.45, H 4.94, Mn 3.40, Br 5.40 Required: as (79)	627. (EI I070) Relatively intense peaks found at m/e = 447,263(PPh_3^+). No obvious fragmentation pattern. No N thus Mn/CO/PPh /Br complex or organic material
82	Triphenyl-carbinol	Toluene NEt_3 70	2090(v.s.),2030 (v.s.),2000(v.s., broad),I960(v.s., broad).Little changed from intermediate.	C 64.84, H 4.I2, Mn 6.66, Br 9.22 $[Mn(CO)_4(PPh_3)(OCPh_3)]$ requires C 7I.5I, H 4.36, Mn 7.99 $Mn(CO)_4(PPh_3)Br$ requires C 5I.87, H 2.95, Mn I0.8I Br I5.76	
83	"	Toluene NEt_3 I00	2085(m),20I0(w), I985(m),I950(v.s.)	C 78.52, H 5.32, Mn 3.50, Br 2.52 Required: as (82)	523, requiring a monomer or higher oligomer. Relatively intense peaks found at m/e= 447,429($Mn(CO)_4(PPh_3)^+$),367, 263(PPh_3^+),243($Mn(CO)_3(OCPh)^+$)

84	Ethanediol	Toluene NEt_3 70	2080(m),20I0(sh), 2000(s),I940(s, broad)	C 64.30, H 4.37, Mn 6.0I, Br 7.84 $[Mn(CO)_3(PPh_3)(OCH_2CH_2OH)]_2$ requires C 59.74, H 4.33, Mn II.90 $[Mn(CO)_2(PPh_3)(OCH_2CH_2OH)]_n$ requires C 60.83, H 4.6I, Mn I2.67	580, requiring at least a dimeric complex. Relatively intense peaks found at m/e=447, 370,305,279,263(PPh_3^+),I83(PPh_2^+) No obvious fragmentation pattern
85	"	Toluene NEt_3 I00	2060(w),2020(w), I952(s,broad),I9I5 (m,broad)	C 7I.76, H 5.32, Mn 4.34, Br 0.88 Required: as (84)	960, requiring at least a trimeric complex. A relatively intense peak was found at m/e= 263(PPh_3^+).No obvious fragmentation pattern.

CHAPTER 4

RESULTS AND DISCUSSION

The experimental work carried out in this study has been concerned with the preparation of alkoxy derivatives of manganese carbonyl. Initial work involved the reactions of $Mn(CO)_5Br$ with the alcohols ethane 1,2 diol, 2-chloroethanol and ^{t}butanol and also with water, and the reaction of the phosphine intermediate $Mn(CO)_4(PPh_3)Br$ with ethanol, 2-chloroethanol and ^{t}butanol. The preparative route used was the reaction of the carbonyl complex with the alcohol in a hydrocarbon solvent in the presence of a base (triethylamine). Due to unreliable and non-reproducible results, optimization of the reaction conditions was undertaken, changing the base and solvent, and replacing the bromide starting material with the chloride. The result of this work was an improved and more reliable method of preparing the alkoxy derivatives from the reaction of $Mn(CO)_5Br$ with a variety of alcohols in acetone solution and in the presence of sodium carbonate as the base. Further reactions of alcohols with the phosphine intermediate were carried out in toluene solution and with triethylamine as the base (as before). Attempts have been made at purification of the products as described in the preceding chapter. Starting material is found to be present in almost all samples after initial purification, and is difficult to separate due to the chemical similarities between it and the products.

Tables 1-5 collect the experimental data together for each group of reactions carried out, and this section is divided so as to present the results of the sections described in Chapter 3.

A General Aspects

Infra-Red Spectra

The reactions in this study were monitored using IR solution spectra in the carbonyl stretching region, 2100 - 1500 cm^{-1}. These vibrations are quite intense and relatively well isolated from other types of vibration likely to be present. Terminal CO in neutral molecules have stretching frequencies in the region 2100 - 1850 cm^{-1}, μ_2-CO in the region 1860 - 1700 cm^{-1} and μ_3-CO below 1750 cm^{-1}.

In compounds containing terminal CO ligands the electron donor properties of other ligands are reflected in the frequencies of the CO stretching vibrations. The greater the electron density supplied by the metal and other ligands, the greater can be the back donation into the π^* orbitals of CO and hence the lower will be the CO bond order and the stretching frequency. Increasing positive charge on the metal decreases the CO stretching frequency. The more electronegative the other ligands in the complex the less electron density is available for back donation to CO and the higher the stretching frequency. PPh_3 is mainly a σ-donor but has vacant π orbitals capable of accepting electron density from filled metal orbitals. The more electronegative the R group of PR_3, the more the ligand mimics CO, and so the phosphine is in effective competition for the back-donated electrons from the metal. This in turn serves to increase the CO stretching frequency. Unlike many ligands in organometallic chemistry, alkoxide is potentially a strong π donor rather than a π-acceptor and therefore the presence of an alkoxide ligand results in a lowering of the CO stretching frequency by not competing for electrons with the CO π^* orbitals [1].

The number of bands in the IR spectrum is diagnostic in terms of structural identification. In general, the more symmetric a molecule the fewer IR active CO normal modes of vibration and the fewer bands seen in the spectrum. From the work of Abel [2] trimeric alkoxy-derivatives of the type $[Mn(CO)_3(OR)]_3$ (Fig. 4.1) exhibit nine active CO bands whilst the tetrameric $[Mn(CO)_3(OR)]_4$ (fig. 4.2) exhibits only three.

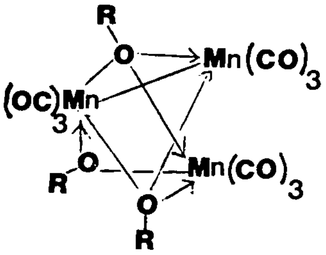


Figure 4.1

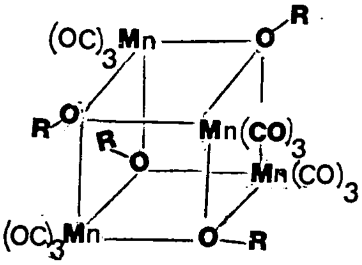


Figure 4.2

Abel recorded the IR spectra in hexane solution, there being no hexane absorptions in the carbonyl stretching region. The toluene solutions used in the study have the disadvantage of toluene absorptions in the region of interest, in particular a strong absorption at approximately 1940 cm^{-1}. Acetone does not affect spectra in the carbonyl regions but with both solvents quite broad peaks were found and these may be obscuring fine structure.

^{1}H nmr Spectra

Relatively few nmr spectra could be collected due to solubility problems, the reaction products being reluctant to dissolve in $CDCl_3$ or d_6-acetone, even though readily soluble in the non-deuterated solvents. Despite forming strongly coloured yellow solutions, less than 10% of the added solid actually dissolved making it often impossible to detect product peaks in the spectra, or to assign any peaks found not to be due to TMS or solvent. Since the presence of any starting material ($Mn(CO)_5Br$) in the product does not affect the ^{1}H nmr spectra these spectra would have been able to yield useful information about the nature of the alkoxide groups present. The ^{1}H nmr spectra of the purified samples 1 and 3 (a phosphine/ethanol product in the combined products of the $Mn(CO)_5Br$/2-chloroethanol reactions) in d_6-acetone showed shifts of solvent bands of approximately 1 ppm, similar to the shift found for the methoxy derivative (73) in d_6-acetone, due to the presence of paramagnetic components, most probably of the type $[Mn(OR)_2]_n$. The components may well be present in varying amounts in all the product samples.

These shifts can be used to derive important information such as the magnetic susceptibility of the paramagnetic materials. The commonly used method for this is known as the Evans' Method [3,4].

Mass Spectra

The mass spectra obtained proved useful in establishing the likely products of the reactions, although no obvious fragmentation patterns were evident in many cases due to the general thermal instability of manganese carbonyl compounds at the operating temperature of the mass spectrometer. It is difficult to say for certain that the highest m/e recorded is of the parent molecular ion, or a fragment of it, and overloading of some of the samples made interpretation more difficult.

Few studies have been carried out on transition metal compounds containing alkoxide ligands but data is available for the corresponding thiols. $Mn_2(CO)_8(SR)_2$ compounds (R = Et, Bu^n) fragment by successive loss of all CO groups to give $Mn_2(SR)_2{}^+$ ions, with the metal-sulphur entity remaining intact. This was followed by loss of R groups. The trinuclear rhenium compound $Re_3(CO)_9(PPh)_3$ and the tetrameric $Mn_4(CO)_4(SR)_4$ (R = Et, Bu^n) behaved similarly.

A large number of compounds containing metal-phosphorus bonds have been studied. In mononuclear compounds such as $(Et_3P)Mn(CO)_4Cl$ fragmentation is by successive loss of CO, and $(Et_3P)MnCl^+$ is the base peak. Mn^+ is the only ion not containing a Mn-P bond. The binuclear species $[(R_3P)Mn(CO)_4]_2$ (R_3 = Et_3, $Pr_3{}^n$, $Bu^n{}_3$, $PhEt_2$, Ph_2Et, Ph_3) shows a large number of ion peaks due to CO losses, usually in low abundance. The base peaks are $(R_3P)Mn^+$ in all cases. The only ions not having a Mn-P bond were Mn^+ and those due to the phosphorous containing ligand, i.e. R_3P^+. A feature of the spectra of many metal-phosphorus compounds is the formation of ions due to cleavage of the R-P bonds. Ions of the types $(R_2P)Mn^+$ and R_2PHMn^+ are found in low abundance in the spectra of all $[(R_3P)Mn(CO)_4]_2$ compounds [5,6].

From the available data in this study it appears that the corresponding manganese alkoxy derivatives fragment by loss of CO and OR groups i.e. OR groups are lost before all COs. In a number of cases oligomeric units broke down to give mononumeric or dimeric fragments, though usually it was loss of ligands from the parent molecule which could be identified. With triphenylcarbinol and benzyl alcohol it was found that phenyl groups were being lost from the alkoxide ligand. Spectra of the phosphine complexes were in general less informative. In a very small number of cases cleavage of an oligomeric unit into dimeric or monomeric units was observed. $[Mn(CO)_2(PPh_3)]^+$ and $[Mn(CO)_4(PPh_3)]^+$ ions were also detected. The CO and alkoxide ligands appear to be more readily lost than PPh_3, which is found in almost every spectrum as a very intense peak at $m/e = 262$.

Section I

B Reaction of $Mn(CO)_5Br$ with Alcohols

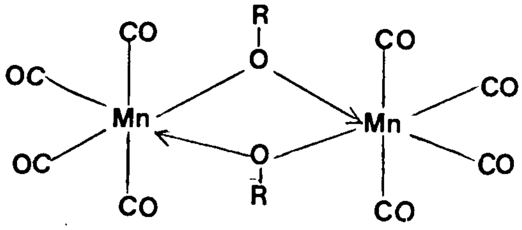
Attempted reaction with ethanediol gave no products and there was little evidence of reaction to be found in the IR spectra. A problem with these reactions is that $Mn(CO)_5Br$ has only limited solubility in hexane and toluene.

Reaction was obtained with 2-chloroethanol and water, but the results were not always reproducible in terms of yields and nature of the products. In the case of ^{t}butanol product isolation caused problems. Commonly the IR spectrum showed reaction to have occurred, but no products could be isolated. A broad peak in the low 1900 cm^{-1} region is common to the reactions in toluene and is probably the result of overlap of bands due to the solvent and the product CO stretching vibrations. The common patterns for the IR spectrum consist of two peaks above 2000 cm^{-1} and one below, with the addition of a peak of varying intensity at approximately 1980 cm^{-1}. This does not seem to be associated with starting material since it is often absent where there is a high proportion of $Mn(CO)_5Br$ still present. In certain spectra it can be observed to disappear with increasing reaction time and therefore is most likely to be associated with some kind of intermediate.

Starting material is present in varying amounts, as indicated by the bromine analyses, together with a small quantity of $[NEt_3H]Br$ in some cases, which may be removed by further extractions with water from dichloromethane solution. The possibility of mixed bromo/alkoxy complexes cannot be ruled out in these reactions.

The IR and mass spectra were correlated to provide evidence for the nature of the products formed. With 2 chloroethanol a mixture of products was obtained, the mass spectral data requiring a dimeric, $[Mn(CO)_4(OR)]_2$, figure 4.3, trimeric tetrameric or higher polymeric unit (in two cases n = 6 or 7) $[Mn(CO)_3(OR)]_n$ (see Table 1).

Figure 4.3 Structure of $[Mn(CO)_4(OR)]_2$



The variation in colour from bright yellow to dark orange is thought to be due to a mixture of oligomers in different ratios. TLC on (10) and (11) gave two spots which may be starting material and products, or separation of a mixture of products, e.g. separation of a dimer from a trimer, which is due to their chemical similarity. The mass spectra indicate some fragmentation by CO loss but no other obvious patterns emerge.

The product obtained from the water reaction depended upon the temperature of the reaction. The mass spectrum of the product obtained at room temperature indicated possibly a dimeric unit, (highest m/e = 390), whilst heating to 55°C appeared to yield a tetramer $[Mn(CO)_3(OH)]_4$ (highest m/e = 592). Initially the IR spectrum of this 55°C reaction corresponded to that of the reaction carried out at room temperature, i.e. three strong peaks at 2030, 1965 and 1920 cm^{-1}, and so the initial reaction may lead to formation of a dimer and more prolonged heating leads to formation of the tetrameric complex.

There appeared to be very little reaction with ^{t}butanol in hexane and the products from reaction in toluene were only obtained in very low yields, with the presence of starting material being indicated, again due to the limited solubility of $Mn(CO)_5Br$ in hydrocarbon solvents. The reaction in acetone yields a tetrameric or hexameric product $[Mn(CO)_5(O^tBu)]_n$, according to the mass spectra obtained (highest m/e values obtained = 683 and 1155).

It appears that prolonging the reaction time and using a high temperature in these reactions may favour formation of higher molecular weight complex.

C Reaction of $Mn(CO)_4(PPh_3)Br$ with Alcohols

The products obtained from these reactions were in general more difficult to identify positively due to a greater number of variations offered by the presence of the PPh_3 ligand. There is the possibility of bromo and/or alkoxy bridging groups, one or two PPh_3 ligands being incorporated into the oligomers at higher temperatures and also the possibility of obtaining complexes containing only Mn, CO and PPh_3, and no alkoxide ligand. The phosphine intermediate $Mn(CO)_4(PPh_3)Br$ was found to be present in all products (as indicated by the bromine analysis), though generally less than the presence of starting material $Mn(CO)_5Br$ in the above reactions.

With ethanol at 80°C yellow products were obtained. The mass spectra indicated m/e values corresponding to dimeric compounds (Figure 4.4) in two cases, (29) m/e = 447 and (30) m/e = 706, and a trimeric unit $[Mn(CO)(_2(PPh_3)(OEt)]_3$ (fig.4.5)

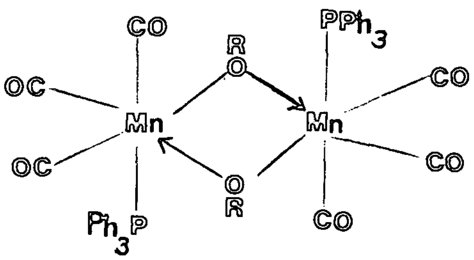


Figure 4.4

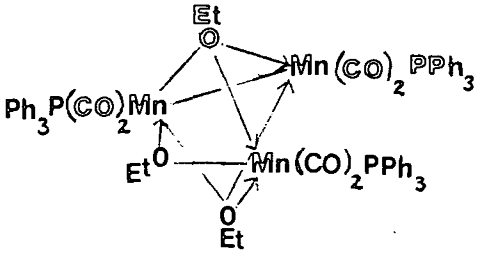


Figure 4.5

The highest m/e value for reaction (32) is 1196, indicating formation of a yellow trimeric complex at 100°C. However, it seems most likely that the light brown product of reaction (31) is $Mn(CO)_3(PPh_3)Br$ as the two peak positions in the IR spectrum (1943, 1915 cm^{-1}) correspond to those of this complex as prepared by Abel [4]. However, the IR spectrum of (32) is almost identical to that for $Mn(CO)_3(PPh_3)_2Br$ and it is difficult to state with certainty whether both reactions have yielded the same product mixed with differing amounts of an intermediate complex, or whether the mixture is of $Mn(CO)_3(PPh_3)_2Br$ with an alkoxy-derivative.

With 2-chloroethanol reaction (34) yielded a bright yellow product with an IR spectrum having peak positions little changed from those of the phosphine intermediate (2080, 1990, 1950 cm^{-1}), but of lower intensity. It is possible that this intermediate, $Mn(CO)_4(PPh_3)Br$, or an alkoxy derivative could have been the product isolated. However, reaction at the same temperature, and at 100°C, gave an IR spectrum consisting of a single strong peak at 1945 cm^{-1}. The cream solid isolated from reaction (36) is organic material as the manganese content is negligible. It appears that at higher temperatures the alcohol is degrading or is reacting with the base rather than simply losing a proton. ${}^tButanol$ yields yellow-orange products at both 80° and 100°C which have similar, simple IR spectra, and which could be dimers (from the mass spectra the highest $^m/_e$ value = 764 (37) and 857 (38)). The steric requirements of PPh_3 and ${}^tBuO^-$ would make the formation of dimeric complexes more likely so as to relieve crowding and strain in the molecule.

With all these reactions the manganese analyses are lower than expected and it appears that the reaction temperatures of 80° and 100°C are too high to yield alkoxy-derivatives, and instead $Mn/CO/PPh_3/(Br)$ complexes are being formed.

Section II

D Optimization of reaction conditions

The reactions of $Mn(CO)_5Br$ with alcohols in acetone gave products with IR spectra similar to those obtained in Section B above. The manganese analyses correspond best with a dimeric product obtained using ethanol and an oligomer $[Mn(CO)_3(OR)]_n$ using 2-chloroethanol. The amount of starting material present (as measured by the bromine analysis) is higher than found in B.

Proton sponge with ethanol gave a product required to be tetrameric $[Mn(CO)_3(OEt)]_4$ at the least (highest m/e value in mass spectrum = 584). A higher molecular weight compound would be expected here because of the absence of steric effects due to the EtO group, and proton sponge is a very powerful base. Sodium carbonate gave dark red crystals of

$[Mn(CO)_3(OEt)]_3$ and the amount of starting material is much lower than with proton sponge.

Using ethanol as solvent as well as reactant yields yellow products, having m/e values in the mass spectrum which require the presence of at least a trimeric complex (m/e = 538 (41) and 447 (42)). With proton sponge as the base a great deal of starting material and also of protonated proton sponge (as seen from the nitrogen analysis results) is present. The product obtained from this reaction darkened from yellow to brown due to aerial oxidation. A Mn(III) species may be formed as the brown colour is usual for this oxidation state as this type of oxidation has been noted before in the preparation of simple alkoxides of manganese [8].

The reaction of $Mn(CO)_4(PPh_3)Br$ with ethanol at 70°C using proton sponge gives a product with a very low manganese content and with an IR spectrum similar to those found for the analogous reactions with 2-chloroethanol in B. From the mass spectrum it appears that the product obtained is mostly proton sponge as the most intense peak is found at m/e = 214, it molecular mass. At 100°C the IR spectrum corresponds to that of the reactions with ethanol at the same temperature described in B having bands at 2060, 1955 and 1915 cm^{-1}. The mass spectrum requires a minimum of a dimeric complex to be present (highest m/e = 637), although the analyses show the manganese content to be very low. There was also aerial oxidation of the product to give the brown colour common to

Mn(III) compounds.

With sodium carbonate at 70°C the IR spectrum is quite complex and the mass spectrum requires at least a trimeric complex to be present (highest $^m/_e$ = 970). At 100°C the IR spectrum is reduced to a single major peak at 1955 cm^{-1} and the mass spectrum requires a dimeric complex (highest $^m/_e$ = 577). In all these reactions the manganese content is lower than expected but the amount of the phosphine intermediate present (as measured by the bromine analysis) is very low (less than 3% bromine).

The reactions with $Mn(CO)_5Cl$ did not prove to be any faster than with the bromide, nor did the reactions go to completion, i.e. starting material was still present (as indicated by halide analysis). The reaction with ethanol yielded a higher molecular weight oligomer, $[Mn(CO)_3(OEt)]_n$ with n > 5 from the mass spectrum, the highest $^m/_e$ value being 834. The reaction of the phosphine intermediate $Mn(CO)_4(PPh_3)Cl$ with ethanol at 70°C gave an IR spectrum similar to those of the corresponding bromide reactions in B. The mass spectral evidence suggests at least a dimeric complex $[Mn(CO)_3(PPh_3)(OEt)]_n$ (the highest $^m/_e$ value is 464).

From the results of these studies several conclusions were made as to the optimum reaction conditions. Acetone is a much better solvent than the hydrocarbons, all reactants being readily soluble and it is easy to remove at the end of the reaction. However, because of its low boiling point it is not suitable for the phosphine reactions, where toluene was retained. A higher ketone could have been used for these reactions but if the boiling point is too high it becomes difficult to remove the solvent at the end of the reaction, and also if the molecular weight is too high, solubility of the reactants decreases.

Sodium carbonate was the preferred base for the non-phosphine reactions as it appears to lead to a greater proportion of the starting material reacting and it can easily be removed from the reaction mixture by filtration. Proton sponge is more difficult to remove and also may be too strong a base to use here. The products from reactions using proton sponge appear to be unpredictable and non-reproducible. Both bases appear less suitable than triethylamine for the phosphine reactions for the reasons given above.

Sodium carbonate has been used in the preparation of alkoxy-derivatives of transition metals, for example:

$\mathrm{xs[RuCl_2(arene)]_2 + Na_2CO_3 + H_2O \longrightarrow [(arene)Ru(OH)_3(arene)]}$ [9]

and

$\mathrm{[Ir(C_8H_{12})Cl]_2 + Na_2CO_3 + ROH \longrightarrow [(Ir(C_8H_{11})(OR)]_2]}$

R = Me,Ph.

It is therefore reasonable to expect reaction to occur with $\mathrm{Mn(CO)_5Br}$.

Ethanol as a solvent gave a great deal of unreacted starting material with proton sponge as base, and although reaction was improved with sodium carbonate the analyses were not in good agreement with the expected results. This method of using the alcohol as both solvent and reactant is not suitable for all the alcohols used in this study, as an alternative solvent must be found for the solid alcohols and also for the very viscous poly-ols. It is also more difficult to dry the alcohols than it is to dry toluene for example, and solubility is lessened with a high molecular weight alcohol.

There appeared to be little difference in rate of reaction of the $Mn(CO)_5Cl$ complex as compared with $Mn(CO)_5Br$. The chloride is also light sensitive and obtaining pure samples in good yields is not as easy as with the bromide.

E Further reactions of $Mn(CO)_5Br$ with Alcohols

All the reactions in this section were carried out using acetone as the solvent and sodium carbonate as the base.

All the alcohols used in this section gave products which are generally oligomeric. The IR spectra were of two basic types as in Section B, (i) two peaks between 2000 cm^{-1} and 2100 cm^{-1} and one between 1900 and 1970 cm^{-1}, or (ii) a single peak at each of the previous positions, with or without a peak at 1980 cm^{-1}. As described in Section B, this last peak is believed to be due to a distinctly separate component rather than being due to starting material, since it is often absent where the bromine analysis is quite high and for products having approximately equal bromine analyses the intensity of the peak can vary greatly. The colours of the products are mostly yellow, with several orange compounds. Butan-1-ol yielded a dark red/brown solid.
The products obtained from reactions of this alcohol, (53)

and (56), turned brown on standing and it is most likely that aerial oxidation to Mn(III) has taken place. Products from reactions with water, acetoxime, ethanediol and glycerol (one of two reactions in the latter two cases) were brown in colour and this is probably the result of oxidation to Mn(III), though the analysis results for the acetoxime product in particular are close to those required for a dimer $[Mn(CO)_4(ON{=}CMe_2)]_2$, which is in agreement with the mass spectral data (highest $^m/_e$=335). In most cases a single reaction was carried out with an alcohol and so it is more difficult to state for certain whether the product is a mixture of one product and starting material or several oligomers and starting material. Repeat reactions were carried out with ethanol, 2-chloroethanol, water, ^{t}butanol propan-2-ol, glycerol and 2 butyne-1,4-diol. Both ethanol reactions gave high molecular weight complexes, n = 6 in $[Mn(CO)_3(OEt)]_n$ from the mass spectral data (highest values = 987 (51) and 1105 (52)), but the amounts of starting material and the colours of the products differed, the yellow product of (52) being heated for 18 hours longer than (51). With 2-chloroethanol the products obtained are the same colour and both are dimeric (from mass spectral data, highest $^m/_e$ = 446 (53) and 278 (54)), with similar amounts of starting material present. Products of different colours were obtained with water, glycerol and 2 butyne-1,4-diol but lack of data for the second reaction product makes comparison more difficult, although the IR spectra were quite similar. ^{t}Butanol yields yellow products from both (57) and (58), but the amount of starting material in (58) is half that of (57) and the mass spectral data indicates a minimum of a trimer for (58) (highest $^{m}/_{e}$ = 503) and a tetramer for (57) (highest $^{m}/_{e}$=834). It could be that these products are identical (as are their IR spectra) and that fragmentation in the mass spectrometer has prevented detection of the highest weight oligomer in (57). With propan-2-ol an orange product is obtained in (59) for which the mass spectral data requires at least a tetrameric complex (highest $^{m}/_{e}$ value = 609). However, heating for a further 20 hours (60) produced a dark yellow compound which was required to be trimeric (highest $^{m}/_{e}$=535). Double the amount of starting material was present here as compared to (58).

In this series of reactions the main products are trimeric $[Mn(CO)_3(OR)]_3$ complexes, if the mass spectral data are taken to refer to the parent molecule. A monomeric complex is obtained with triphenylcarbinol (highest $^{m}/_{e}$ value in mass spectrum = 410), as might be expected considering that it has one of the highest pK_a values, i.e. is less reactive toward proton loss, and it is also a very sterically demanding group. A group of this size would find bridging two or more manganese atoms impossible due to repulsions and the inherent strain in such a complex.

Dimeric complexes were obtained with 2-chloroethanol, and acetoxime, but tetrameric complexes with ^{t}butanol, propan-2-ol and 2-methoxyethanol.

Ethanol gave hexameric units, and in the case of methanol and ethanediol, oligomeric complexes of high molecular mass were obtained (highest $^{m}/_{e}$ = 685 for methanol and 1058 for ethanediol). Because it is not certain that the parent molecular ion is being detected in each case, it is possible that what are being detected are fragments of oligomer units of higher molecular mass. However in some cases, such as triphenyl carbinol for example, the oligomer detected in the mass spectrum is most likely to be of the "correct" cluster size. It would appear that the products obtained are mixtures of one complex and starting material in general (although formation of mixed bromo alkoxy complexes cannot be ruled out). The reactions with glycerol and ethanediol are most likely to have yielded complexes with the alcohol bonded via only one oxygen atom, rather than as a chelate, since the amount of base added was only equivalent to the removal of one proton, and it is unlikely that a double (or triply charged (in the case of glycerol)) alkoxide entity would be produced or be sufficiently stable in these conditions.

The ^{1}H nmr of the methoxy derivative in d_6-acetone solution showed a shift in solvent and reference peaks of approximately 1 ppm, due to the presence of paramagnetic material, such as for example $[Mn(OMe)_2]_n$. The presence of this material leads to speculation as to whether the other products will also contain this type of paramagnetic alkoxide.

F. Further Reactions of $Mn(CO)_4(PPh_3)Br$ with Alcohols

These reactions were in general the most difficult to interpret with any great certainty and were also the most unsatisfactory in terms of products obtained.

The IR spectra vary quite widely, and relate to the amounts of the phosphine intermediate ($Mn(CO)_4(PPh_3)Br$) present. This contamination however in less than the amounts of $Mn(CO)_5Br$ present in the products of the reaction not involving phosphines (as measured by the bromine analysis). The mass spectral data, if taken as recording the parent molecular ion, show that monomeric or dimeric complexes are obtained (see Table 5), except in the case of the reaction with ethanediol at 100°C, (which produces a trimeric complex), which would perhaps be expected due to its greater acidity and hence greater reactivity, and since steric factors become more important with the bulky phosphine group present.

The analysis results are generally low, especially those for manganese, and it is likely that products are mixed with not only the starting material (phosphine intermediate) but also some with (an)other manganese/CO/PPh_3 complex(es). Reaction with acetoxime yielded orange products in all cases except (75), when reaction using sodium carbonate at 100°C gave a pale brown solid, possibly $Mn(CO)_3(PPh_3)_2Br$. No nitrogen was found in the products of reactions (74) and (75) and its content in (78) is very low. With the base, sodium carbonate, being insoluble in toluene there may be problems in getting reaction with the alcohol. The analysis results for manganese content are again lower than expected.

p-Nitrophenol yielded yellow-green complexes. The reaction at 70^{o}C gave a monomeric complex (highest $^{m}/_{e}$ value in the mass spectrum = 502), with low analyses for manganese and nitrogen. These values are even lower in the case of reaction at 100^{o}C (80), and there is no nitrogen present in reaction (81). It seems likely that a Mn/CO/PPh_3(Br) complex of some kind is the main product of these reactions, with some alkoxy derivative being formed in the reaction at 70^{o}C. The nitrogen containing compound can be p-nitrophenol and/or $[NEt_3H]Br$. Steric factors may be more important here, with triphenyl phosphine and p-nitrophenol both being sterically demanding. The IR spectra of (79) and (81) show peaks at the same frequencies as $Mn(CO)_4(PPh_3)Br$ though of lower intensity.

The products obtained from reactions at the two temperatures using triphenylcarbinol gave compounds of different colours. At 70^{o}C a bright yellow compound was obtained whose IR spectrum contained CO stretching vibrations at the same frequencies as those of the phosphine intermediates but of lower intensity (2090, 2030, 2000 and 1960 cm^{-1}). It would appear that this could be the major product isolated, with possibly some monomeric alkoxy derivative. This would be in line with the steric considerations, Ph_3CO^- having a considerable molecular volume. The presence of PPh_3 will also consign the alkoxy complex to a monomer. Triphenol carbinol is also a weak acid and so will be less reactive towards alkoxide ion formation.

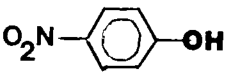
At 100°C an orange solid was obtained and the IR spectrum indicates more reaction. Some intermediate remains (from the bromine analysis), but there is the possibility of a Mn/CO/PPh_3 complex being present as well as the alkoxy derivative which appears to be a monomer for the reasons stated above.

The reaction of ethanediol with the phosphine intermediate complex proceeds as with triphenyl carbinol at the same temperature. A yellow solid is obtained which has an IR solution spectrum very similar to the intermediate (bands at 2080, 2000 and 1940 cm^{-1}). The mass spectrum indicates a higher mass unit than in previous cases and thus the product is most likely to be a mixture of phosphine intermediate, alkoxy-derivatives $[Mn(CO)_3(PPh_3)(OCH_2CH_2OH)]_2$ (minimum required by mass spectral data where the highest m/e value is 580) and Mn/CO/PPh_3 complex.

At 100°C the bromine analysis on the product shows trace amounts only of the intermediate (confirmed by the IR spectrum) and on the yellow product is most likely to contain the alkoxy derivative $[Mn(CO)_2(PPh_3)(OCH_2CH_2OH)]_3$ (minimum required by mass spectral data (highest m/e value = 980) and a Mn/CO/PPh_3 complex. The diol is likely to be bonded via only one of its oxygen atoms since only one proton equivalent of base was added, and formation of the anion would require a much stronger base. The likelihood of a dimeric or trimeric alkoxy compound is enhanced by the greater acidity of ethanediol, as compared to the simple alcohols such as ethanol, though this has to be balanced against a reduced tendency to bond to the metal with high acidity.

The likely products and rate of reaction can be accounted for by consideration of the acidity of the alcohols concerned. The aliphatic alcohols are weak acids, having pK_a values higher than that of water (15.7) with the exception of methanol, although acidity is often higher in aromatic alcohols e.g. phenol $pK_a = 10$. Table 4.1 lists pK_a values of some of the alcohols used in this study. The higher the pK_a value, the weaker the acid [11].

Table 4.1

Alcohol	pK_a (25°C)
EtOH	16
H_2O	15.7
$(CH_2OH)_2$	15.4
MeOH	15
$CH_3OCH_2CH_2OH$	14.8
$CH_2OH.CHOH.CH_2OH$	14.4
CH_2ClCH_2OH	14.3
	7.2

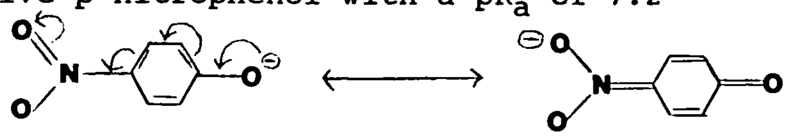
Since an alcohol contains a proton bonded to very electronegative oxygen appreciable acidity would be expected since loss of the proton leaves a negative charge which can be easily accommodated by the oxygen atom. However, not all alcohols have the same acidity and the magnitude of the pK_a value will depend on the other functional groups present (as demonstrated in Table 4.1). Three structural effects determine the stability of the conjugate base (the alkoxide ion) and hence the acidity: (i) inductive effects. A σ-bond can be polarised by the influence of an adjacent polar bond or group. For example, in 2-chloroethanol, the electronegative chlorine atom attracts electron density from the carbon atom to which it is bonded and creates a permanent dipole

$$\overset{\longleftarrow\!\!+}{Cl - CH_2}\overset{\longleftarrow\!\!+}{\ - CH_2} - OH$$

This C - Cl dipole influences the adjacent carbon atom by an electron-withdrawing inductive effect. The effect weakens with distance between interacting groups. It serves to stabilize the $ClCH_2CH_2O^-$ anion (the conjugate base) and hence it will be more acidic than CH_3CH_2OH, where there is no such effect.

(ii) Steric effects. Steric hindrance to solvation caused by the bulk of the acid or the solvent can inhibit solvent stabilisation of the conjugate base and thereby lower acidity. Such groups as ^tBu- and Ph_3C- will prevent the close approach of solvent molecules to form the necessary interaction between them and the conjugate base so that ^tBuOH and Ph_3COH will be weaker acids than EtOH.

(iii) Resonance effects. Where it is possible to delocalize the negative charge of the alkoxide ion, and hence stabilize it by resonance, the acidity of the alcohol will be increased. This effect is well illustrated by the phenolic derivative p-nitrophenol with a pK_a of 7.2



The presence of an aromatic ring does not automatically bring resonance stabilisation however. Benzyl alcohol $PhCH_2OH$ is a good example - the aromatic ring is remote from the oxygen atom and resonance stabilisation is impossible.

Within a series of aliphatic alcohols the larger the alkyl group, the weaker the acid. Methanol is the strongest acid, tertiary alcohols are the weakest. This is due mainly to solvation effects - a bulky group interferes with the ion-dipole interactions which stabilized the anion [12].

The most acidic alcohols used in this study were p nitrophenol and acetoxime and these were found to have the most facile reactions (non-phosphine), with reaction times being the shortest. In general the trend observed is for a longer reaction time to be required for the weaker acids, the longer chain aliphatics, e.g. butan-1-ol, and the more sterically hindered tertiary alcohols such as ^{t}butanol and triphenyl carbinol.

In general the reactions employing sodium carbonate as the base took slightly longer than those using triethylamine, presumably because the former is insoluble in acetone.

In view of the increasingly rich chemistry of transition metal alkoxide complexes and alkoxy derivatives it seems surprising that a greater number of manganese complexes of this type have not been prepared. The first alkoxy carbonyls of manganese were reported in 1979 by Abel [2] but since then relatively little work has been carried out in this field (see Chapter 2).

Abel chose to use the method of reacting a manganese carbonyl halogen compound with base and alcohol which is not commonly used in preparation of transition metal alkoxy derivatives. Some examples of its use are:

$ReOCl_4$ + tertiary amine in methanol $\longrightarrow Re_2O_3(OMe)_6$ [13]

$PhN = WCl_4 + {}^{t}BuNH_2 + MeOH \longrightarrow PhNW(OMe)_4$ [14]

It is more commonly used in the preparation of simple alkoxides, e.g.

$TiCl_4 + 4ROH + 4NH_3 \longrightarrow Ti(OR)_4 + 4NH_4Cl$ [15]

Abel reports reaction with ethanol, low and erratic yields with ${}^{i}PrOH$ and ${}^{n}BuOH$, and no reaction with other alcohols. In his 1983 review of transition metal alkoxides [16] Metrotra expresses surprise at this lack of reaction. In fact Abel successfully obtained trimeric alkoxy derivatives with a number of alcohols, ROH where R = Me, Et, ${}^{n}Pr$, ${}^{i}Pr$, ${}^{n}Bu$, C_6H_{11}, $CH_2CH = CH_2$ or CH_2Ph, by reaction of the trimethyltin derivative with $Mn(CO)_5Br$.

From the results of this study it appears that the main problem with Abel's method is the choice of solvent, i.e. hexane. Early work in the present study also obtained low and unreproducible yields, or no reaction at all, when using hexane, and to some extent toluene, as the solvent. The use of acetone as solvent greatly facilitates reaction, as $Mn(CO)_5Br$ has only limited solubility in hydrocarbons, but is more readily soluble in other organic solvents. Reaction was obtained with a wide range of alcohols and trimeric products appeared to predominate, although the increased solubility of starting material and products in acetone may allow the production of oligomers of high mass. Sodium carbonate or triethylamine can be used as the base, the former being insoluble in acetone which leads to a slightly greater amount of unreacted starting material among the products, though it is much easier to remove from the reaction mixture. Further purification of the products obtained followed by fractional crystallisation or chromatography on basic alumina (cf. Abel [2], the separation of $[Mn(CO)_3(OCH_2Ph)]_3$ and $[Mn(CO)_3(OCH_2Ph)]_4$) should lead to separation of the components of the product mixture. Further work of interest would be the reactions with compounds containing bonds other than C-O such as P-O, B-O, and S-O.

The reactions of alcohols with the phosphine intermediate $Mn(CO)_4(PPh_3)Br$ were less satisfactory. The products appear to be mixtures of this material, a $Mn/CO/PPh_3$ complex and the alkoxy derivative. In some cases the main product isolated was $Mn(CO)_3(PPh_3)_2Br$. It may be easier to obtain products containing other useful ligands such as phosphine, halogen etc. by following the method of Abel [2] and reacting the appropriate reagent with an alkoxy carbonyl derivative:

$$[Mn(CO)_3(OEt)]_3 + PMe_2Ph \longrightarrow [Mn_3(CO)_8(PMe_2Ph)(OEt)_3] + CO$$

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Table 1 Summary of Reactions of $Mn(CO)_5Br$ with Alcohols

Reaction	Alcohol	IR Main Peaks $\nu(CO)\,cm^{-1}$	Mass Spectrum: Highest $^m/e$ value, Minimum oligomer species required, other fragments found	Colour of Product	Other Data
6	2 Chloro-ethanol	2080(m),2040(m), 2030(s),1985(w), 1925(s)		Orange	'H nmr $COCl_3$ solution: singlet at 1.25 ppm
7	"	2030(s),2010(s), 1910(s)	759; Tetramer	Orange	'H nmr $CDCl_3$ solution: Singlet at 1.25 ppm
8	"	2005(s),1900(s)	480; Dimer	Bright Yellow	
9	"	2080(w),2040(m), 2010(s),1985(m), 1915(s)	723; Tetramer	Bright Yellow	
10	"	2030(s),1010(s), 1910(s)	1094; Hexamer	Yellow-orange	
11	"	2050(m),2040(s), 2020(m),1980(w), 1940(s)	833; Pentamer	Orange	
15	"	2080(w),2030(s), 2010(s),1905(s)	603; Trimer	Dk. Orange	
17	"	2030(s),2010(s), 1940(s)	1370; Heptamer	Bt. yellow	
19	Water	2030(s),1965(s), 1920(s)	390; Dimer	Bt. yellow	
21	"	2020(s),1915(s)	592; Tetramer	Yellow	
27	^{t}Butanol	2025(s),2010(m), 1970(m),1925(s)	683; Tetramer $[Mn(CO)_3(O^tBu)]^+$ 1155; Hexamer	Dk. Orange	Acetone solvent

All reactions: Solvent - hydrocarbon; Base - NEt_3

Table 2 Summary of Reactions of $Mn(CO)_4(PPh_3)Br$ with Alcohols

Reaction	Alcohol	IR Main Peaks ν(CO) cm^{-1}	Mass Spectrum: Highest $^m/e$ value, Minimum oligomer species required, other fragments found.	Colour of Product	Other Data	Reaction Temp.
29	Ethanol	2085(m),1990(s), 1950(s).	447; Dimer	Bt. yellow		
30	"	2010(w),1990(s), 1950(s)	706; Dimer	Dk. yellow	^1H nmr $CDCl_3$ solution: Singlet 1.57ppm; singlets at 7.38,7.46,7.63 and 7.75ppm (PPh_3)	80°C
31	"	1943(s),1915(s)	837; Dimer	Lt. brown	^1H nmr $CDCl_3$ solution: singlet 1.57ppm; singlet 7.33ppm and multiplet 7.55ppm (PPh_3). Probably $Mn(CO)_3(PPh_3)_2$ Br from colour and IR bands	100°C
32	"	2060(w),1955(s), 1915(s)	1196; Trimer $[Mn(CO)_3(PPh_3)(OEt)]^+$	Bt. yellow	^1H nmr $CDCl_3$ solution: singlet at 1.57 ppm. Doublet 7.33,7.39 ppm, two multiplets 7.54 and 7.75 ppm (PPh_3)	80°C
33	"	2085(m),2005(s), 1945(s)	1103; Trimer $[Mn(CO)_4(PPh_3)(OEt)]^+$	Yellow	^1H nmr $CDCl_3$ solution: singlet at 1.57ppm. Singlets 7.38 and 7.46 ppm and a multiplet 7.75 ppm (PPh_3)	
34	2 Chloroethanol	2080(m),1990(m), 1950(s)	808; Dimer $[Mn(CO)_4(PPh_3)]^+$, $[Mn(CO)_2(PPh_3)]^+$	Bt. yellow		80°C

36	2 Chloro-ethanol	1990(w),1945(s), 1918(w)	633; (Dimer) $[Mn(CO)_2(PPh_3)(OR)]^+$ $[Mn_2(PPh_3)(OR)]^+$ $[Mn(CO)_4(PPh_3)]^+$	Cream	Mn,Br content very low. Most probably organic material	100°C
37	^{t}Butanol	2080(w),2999(w), 1990(s),1953(s)	764; Dimer	Yellow-Orange		80°C
38	"	2065(w),1946(s), 1918(s)	857; Dimer	Yellow-Orange		
			PPh_3^+ found in every case.			

All reactions : Solvent - Toluene, Base - NEt_3

Table 3 Summary of Optimization Studies of Reaction Conditions

Reaction	Alcohol	Conditions	IR Main peaks ν(CO) cm^{-1}	Mass Spectrum: Highest $^{m}/e$ value, Minimum oligomer species required, other fragments found	Colour of Product	Other Data
39	Ethanol	Solvent-Acetone Base-NEt_3	2020(s),1973(w), 1915(s)		Orange	
40	2 Chloro-ethanol	"	2025(s),1975(w), 1918(s)		Orange-brown	
41	**Ethanol**	Solvent-Ethanol Base-Proton Sponge	2020(s),2010(m), 1990(s),1920(s), 1890(s)	538; Trimer/906; Tetramer $[Mn(CO)_4(OEt)]^+$	Yellow-brown	Low analysis results. Very high starting material content. Oxidation to Mn^{III} occurring.
42	"	Solvent-Ethanol Base– Na_2CO_3	2030(m),2010(w), 1998(s),1895(s)	447; Trimer $[Mn(CO)_4(OEt)]^+$	Yellow	Mn analysis low
43	"	Solvent-Acetone Base-Proton Sponge	2010(s),1972(s), 1935(s)	584; Tetramer $[Mn(CO)_4(OEt)]^+$ $[Mn(CO)_3(OEt)]^+$	Bt. Yellow	
44	"	Solvent-Acetone Base-Na_2CO_3	2030(s),1972(w), 1920(s)	464; trimer	Dk red xls	
45	"	Phosphine, 70°C Solvent-Toluene Base-Proton sponge	2090(w),2060(w), 2010(w),1990(w), 1952(s)	354; Dimer $[Mn(CO)_4(OEt)]^+$	Orange-brown	Low Mn analysis
47	"	Phosphine 100°C Solvent-Toluene Base-Proton sponge	2060(w),1955(s), 1915(s)	637; Dimer $[Mn(CO)_2(PPh_3)_2]^+$	Yellow-brown brown	Low Mn analysis Oxidation to Mn^{III} accounts for colour change of solid.

46	"	Phosphine 70°C Solvent-Toluene Base-Na_2CO_3	2085(w),2025(m), 2000(m),1990(m), 1950(s),1915(s)	970; Dimer	Orange-brown	
48	"	Phosphine 100°C Solvent-Toluene Base-Na_2CO_3	2040(w),1955(s)	577; Dimer	Bt. orange	Low Mn Analysis
49 $Mn(CO)_5Cl$	EtOH	Solvent - acetone Base - NEt_3	2030(v.s.),1970(w), 1920(v.s.),1863(m)	757,834; Pentamer $[Mn(CO)_3(OEt)]^+$	Dark-orange	
50 $Mn(CO)_5Cl$	"	Phosphine 70°C Solvent-Toluene Base-NEt_3	2085(m),2030(w), 2010(m),1990(s), 1950(s)	464; Dimer	Bt. yellow	

Table 4 Summary of Further reactions of $Mn(CO)_5Br$ with Alcohols

Reaction	Alcohol	IR Main Peaks ν(CO) cm^{-1}	Mass Spectrum: Highest $^m/e$ value, Minimum oligomer species required, other fragments found	Colour of Product	Other Data
51	Ethanol	2038(s),2018(s), 1978(s),1930(s)	987; Hexameric $[Mn(CO)_3(OEt)]^+$	Bt. orange	
52	"	2022(s),1915(s)	1105; Hexameric $[Mn(CO)_3(OEt)]^+$	Yellow	
53	2 Chloro-ethanol	2030(s),2010(w), 1925(s)	446; Dimer	Yellow — brown	Oxidation to Mn^{III} causes colour change
54	"	2035(s),1925(s)	278; Dimer	Dk. yellow	
55	Water	2030(v.s.),1975(w), 1920(v.s.,1860(s)	424; Trimer	Dk. yellow	
56	"	2035(v.s.),1980(w), 1125(v.s.)		Dk. brown	Very low yield
57	^{t}Butanol	2030(v.s.), 1920(v.s.)	834; Tetramer	Yellow — brown	Oxidation to Mn^{III} causes colour change
58	"	2030(v.s.), 1923(v.s.)	503; Trimer	Bt. yellow	
59	Propan-2-ol	2030(v.s.,2010(w), 1972(m),1920(v.s.)	609; Tetramer	Orange	
60	"	2020(v.s.),1905(v.s.)	535; Trimer $[Mn_2(CO)_8(OR)]^+$, $[Mn_2(CO)_6]^+$	Dk. yellow	
61	Butan-1-ol	2040(w),2030(s), 1995(w),1980(w), 1922(s)		Dk. red/brown	Very low yield

62	Triphenyl-carbinol	2010(s), 1975(s), 1925(v.s.)	410; Monomer $[Mn(CO)_3(OCPh)]^+$, $[OR]^+$	Pale yellow	
63	2 Methoxy-ethanol	2030(s), 2010(s), 1915(v.s.)	833; Tetramer	Dk. yellow	
64	Glycerol	2030(m), 2010(v.s.), 1900(v.s.)	535; Trimer	Dk. yellow/ brown	
65	"	2030(m), 2010(v.s.), 1900(v.s.)		Brown	Very low yield
66	Acetoxime	2025(v.s.), 1915(v.s.).	535; Dimer	Brown	
67	p-Nitro-phenol	2030(v.s.), 1925(v.s.)	616; Trimer $[Mn(CO)_3(OR)]^+$, $[OR]^+$	Orange	
68	Benzyl-alcohol	2030(v.s.), 1990(w), 1980(w), 1925(v.s.),	590; Trimer $[Mn(CO)_3(OR)]^+$, $[OR]^+$	Dk. orange/ yellow	
69	3 Buten-1-ol	2030(s), 2010(s), 1975(m), 1925(s)	576; Trimer $[Mn(CO)_3(OR)]_2^+$	Dk. orange	
70	2-Butyne-1,4-diol	2040(s), 2020(s), 2005(w), 1920(v.s.)		Yellow-orange	Very low yield
71	"	2040(s), 2020(s), 1905(v.s.)	466; Trimer	Dk. orange/ brown	
72	Ethanediol	2040(w), 2030(v.s.), 2010(v.s.), 1960(s), 1905(v.s.)	1058; Hexamer or higher oligomer	Brown	
73	Methanol	2035(v.s.), 1930(v.s.)	685; Pentamer or higher oligomer	Dk. orange/ brown	^1H nmr/d_6 acetone 1.2ppm shift of solvent peaks due to para-magnetic material.

All reactions: Solvent : Acetone/Base : Na_2CO_3

Table 5 Summary of Further reactions of $Mn(CO)_4(PPh_3)Br$ with Alcohols

Reaction	Alcohol	Temp.	Conditions	IR Main Peaks $\nu(CO)\,cm^{-1}$	Mass Spectrum: Highest m/e value, minimum oligomeric species required; other fragments found.	Colour of Product	Other Data
74	Acetoxime	70°C	Solvent-Toluene Base-Na_2CO_3	2090(m),2025(s), 2010(m),1945(s), 1922(w),1908(m)	583; Dimer	Bt. orange	No N found
75	"	100°C	"	2000(w),1990(w), 1940(m)	557; Dimer	Pale brown	No N found; Very low Mn. Colour suggests $Mn(CO)_3(PPh_3)_2Br$
76	"	70°C	Solvent-Toluene Base-NEt_3	2025(v.s.),1935(s), 1905(s)	558; Dimer	Dk. orange	
77	"	100°C	"	2080(w),2020(v.s.), 2010(w),1935(s), 1905(s)	555; Dimer $[Mn(CO)_2(PPh_3)(OR)]^+$	Orange	
78	Acetoxime	100°C	Solvent-Toluene Base-NEt_3	2020(w),1990(w), 1941(s),1925(m)	891; Dimer	Bt. orange	Very low Mn and N
79	P Nitro-phenol	70°C	Solvent-Toluene Base-NEt_3	2090(m),2024(w), 2010(s),1950(s)	502; Monomer $[Mn(CO)_4(OR)]^+$ $[Mn(CO)_3]^+$	Dk. yellow/ green	
80	"	100°C	"	2160(w),1990(w), 1947(s)	554; Monomer	Dk. green	Very low Mn analysi
81	"	100°C	"	2080(m),2999(m), 1945(s)	627 1070; Trimer	Dk. yellow/ green	Low Mn analysis No N found.
82	Triphenyl-carbinol	70°C	"	2090(v.s.),2030(v.s.), 2000(v.s.),1960(v.s.)	595; Monomer	Bt. yellow	IR very much like intermediate $Mn(CO)_4(PPh_3)Br$

83	"	100°C	"	2085(m),2010(w), 1983(m),1950(v.s.)	523; Monomer $[Mn(CO)_4(PPh_3)]^+$, $[Mn(CO)_3(OCPh)]^+$	Orange	Low Mn analysis
84	Ethane-diol	70°C	"	2080(m),2999(s), 1940(s)	580; Dimer $[PPh_2]^+$	Yellow	IR very much like intermediate $Mn(CO)_4(PPh_3)Br$
85	"	100°C	"	2060(w),2020(w), 1925(s),1915(m)	960; Trimer	Yellow	
					PPh_3^+ found in almost every case.		