TRIMETHYLPHOSPHINE STABILIZED ALKYLS AND ARYLS OF TRANSITION METALS

A thesis submitted by

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ABSTRACT

The synthesis of trimethylphosphine stabilized σ-alkyl and aryl complexes from the interaction of dialkyl or aryl magnesium reagents with quadruply bonded transition metal acetates is described. Complexes of Cr(II), Mo(II), Ru(II), Rh(I) and Rh(III) have been isolated and in the absence of PMe_3, Re(III) compounds are obtained. The synthesis and properties of a unique triply methylene bridged complex, $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ and some derivatives are also described. The compounds have been characterised spectroscopically (i.r. and n.m.r. (^1H, ^{31}P, ^{13}C)) and the results of some X-ray crystallographic studies are given.

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To My Parents and Sarah

CONTENTS

	Page:
ABSTRACT	2
ACKNOWLEDGEMENTS	3
CONTENTS	5
LIST OF ABBREVIATIONS	6
INTRODUCTION	7
CHAPTER 1 - DIMERIC CHROMIUM(II) AND MOLYBDENUM(II) ALKYLS	8
I. Introduction	8
II. Results and Discussion	9
CHAPTER 2 - ARYLS OF Mo(II), Re(III), Ru(II) AND Rh(I)	15
I. Introduction	15
II. Results and Discussion	15
CHAPTER 3 - DIMERIC RHENIUM(III) ALKYLS	23
I. Introduction	23
II. Results and Discussion	23
CHAPTER 4 - RUTHENIUM(III) METHYLENE BRIDGED COMPOUNDS	28
I. Introduction	28
II. Results and Discussion	29
EXPERIMENTAL SECTION	36
CHAPTER 1	37
CHAPTER 2	47
CHAPTER 3	57
CHAPTER 4	63
REFERENCES	71

List of Abbreviations

Ar	-	aryl
B.M.	-	Bohr Magnetons
Bu^n	-	$-CH_2CH_2CH_2CH_3$
Bu^t	-	$-CMe_3$
F.T.	-	Fourier Transform
i.r.	-	infrared
M.P.	-	melting point
n.m.r.	-	nuclear magnetic resonance
R	-	alkyl
THF	-	tetrahydrofuran
u.v.	-	ultra violet
PhMe	-	toluene

INTRODUCTION

Transition metal σ-alkyls and aryls are now well known,[1,2,3] although few containing strong metal-metal bonds have been reported - examples are $Mo_2(CH_2SiMe_3)_6$ [4] and $Li_4Cr_2Me_8$.[5] The use of trimethylphosphine as a stabilizing ligand in transition metal alkyl chemistry has received relatively little attention possibly due to difficulties in its preparation and handling. This phosphine is a good σ-donor and is much smaller than other bulkier phosphines such as PPh_3 and $PMePh_2$ which are commonly used.[6] Some examples of PMe_3 stabilized methyls can be found in the recent literature; Fe,[7] Co,[8] Ni,[9] Pt,[10] Au,[11] but with aryls and bulky "β-elimination stabilized" alkyls little work has been reported. The interaction of dialkyl or aryl magnesium reagents with quadruply bonded transition metal acetates in the presence of PMe_3 enabling the isolation and characterization of compounds of Cr(II), Mo(II), Ru(II), Rh(I) and Rh(III) and in the absence of phosphine of Re(III) is described in this thesis.

The synthesis and properties of an unusual triply methylene bridged complex $Ru_2(CH_2)_3(PMe_3)_6$ (4.A) and some derivatives, again stabilized by PMe_3, are also described.

CHAPTER 1

DIMERIC CHROMIUM(II) AND MOLYBDENUM(II) ALKYLS

I. INTRODUCTION

Although dimolybdenum(II) tetraacetate, $Mo_2(O_2CMe)_4$, and dichlorodirhenium(III)tetraacetate, $Re_2Cl_2(O_2CMe)_4$, react with methyllithium to give lithium compounds $Li_4[Mo_2Me_8]$ and $Li_2[Re_2Me_8]$ respectively,[12,13] attempts to obtain neutral alkyls from transition metal acetates by action of Grignard reagents led to decomposition; with $Mo_2(O_2CMe)_4$, MgMeI gave a red insoluble pyrophoric substance. However, in the presence of trimethylphosphine the binuclear acetates of Cr(II) and Mo(II) react with magnesium dialkyls,[14] MgR_2, ($R = CH_2SiMe_3$, CH_2CMe_3 for Mo, $R = CH_2SiMe_3$ for Cr) to give neutral, crystalline alkyl derivatives which are dimeric and the metal-metal bond is retained.

For the compounds described here, analytical data is given in Table 1.1, and spectroscopic data in Tables 1.2 and 1.3. Similar reactions also produced the following compounds; $Mo_2Me_4(PMe_3)_4$ (1.E), $Mo_2Me_4(PMe_2Ph)_4$ (1.F), $Mo_2(CH_2SiMe_3)_2((CH_2)_2SiMe_2)(P(OMe)_3)_3$ (1.G), cis-$RuMe_2(PMe_3)_4$ (1.H), $Ru((CH_2)_2SiMe_2)(PMe_3)_4$ (1.I), $Ru((CH_2)_2CMe_2)(PMe_3)_4$ (1.J), fac-$RhMe_3(PMe_3)_3$ (1.K), $Rh(CH_2SiMe_3)((CH_2)_2SiMe_2)(PMe_3)_3$ (1.L).

They are not described in detail in this thesis since they were first made by R.A. Andersen in these laboratories.[15] Further spectroscopic information ($^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ n.m.r.) was obtained for these compounds and this data is included in the Experimental Section.

Dimeric metal-metal bonded alkyls of the Group VI metals previously

known include $W_2(R)_2(NEt_2)_4$, (R = Me, CH_2SiMe_3),[16] $M_2(R)_6$ (M = Mo, W; R = CH_2SiMe_3, CH_2Bu^t) and $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$. The phosphorus ylide compound $Mo_2((CH_2)_2PMe_2)_4$ can also be considered an alkyl.[18]

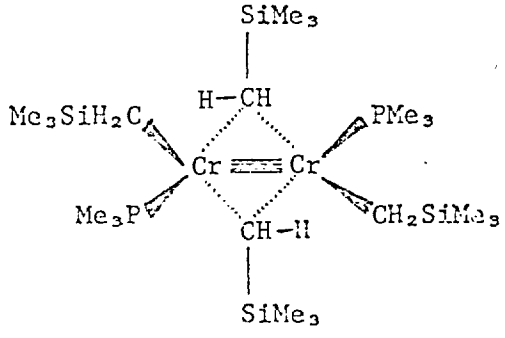
II. RESULTS AND DISCUSSION

1. Chromium Compounds

In diethyl ether at 0°, μ_4-tetraacetatodichromium(II), $Cr_2(O_2CMe)_4$, reacts with $Mg(CH_2SiMe_3)_2$ in presence of PMe_3 to give a dark red pyrophoric dimer of stoichiometry $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ (I.A). The compound has feeble paramagnetism, like other metal-metal bonded chromium(II) species (μ_{eff} ca. 0.9 B.M. per Cr atom in solution), but no electron spin resonance spectrum was observed in frozen benzene at -180° C. The ^1H n.m.r. spectrum showed three rather broad bands of equal area at 35°, which sharpen somewhat at -10° and broaden further on cooling. The $^{13}C\{^1H\}$ spectrum also has three approximately equal peaks but the $^{31}P\{^1H\}$ spectrum had only a single broad peak (δ -17.35) at -80°. The spectra were inadequate to allow structural characterisation but are consistent with the structure (I), determined by X-ray diffraction.[14,19]

The molecule has a short Cr-Cr bond (2.10 Å) corresponding to a quadruple metal-metal bond and two bridging trimethylsilylmethyl groups similar to those found in $[Mn(CH_2SiMe_3)_2]_n$,[20] arranged in a cis configuration with a dihedral angle between the two Cr-C-Cr planes of 101°. There is a slight asymmetry of the Cr-C bridge bonds and also, one of the hydrogen atoms from each bridging CH_2 group shows a close approach (ca. 2.3 Å) to one of the chromium atoms. These features probably result from the packing requirements of the bulky ligands in the crystal.

Similar reactions using other phosphines led to decomposition but by



(I)

Figure (I) X-ray Structure of

$Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ (1.A)

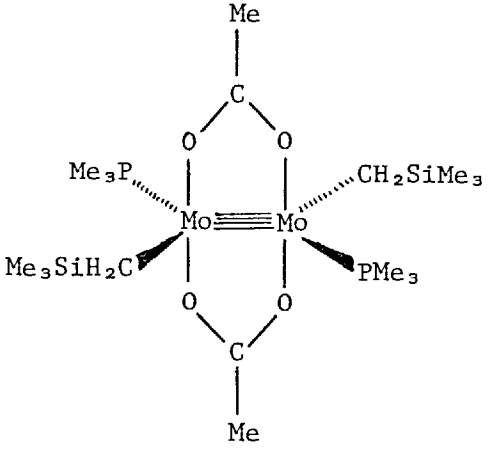
using PMe_3 with $MgMe_2$ and $Mg(CH_2Bu^t)_2$ at 0^o, small yields of extremely pyrophoric petroleum soluble compounds were formed although they were not investigated further.

2. Molybdenum Compounds

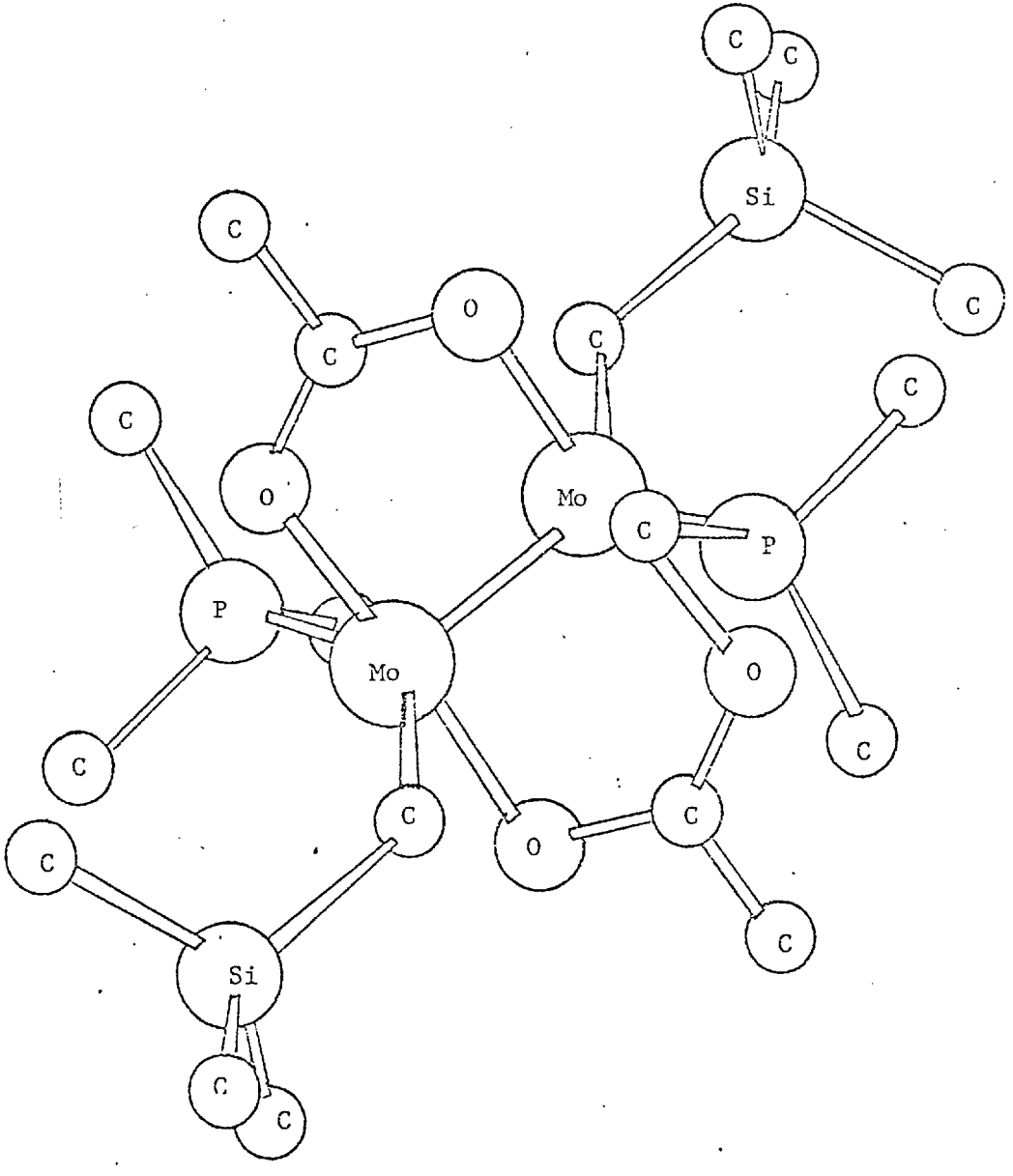
Trimethylsilylmethyl. The interaction of $Mo_2(O_2CMe)_4$ with $Mg(CH_2SiMe_3)_2$ in the presence of PMe_3 gives compound (1.B) that still retains acetate and has formula $Mo_2(O_2CMe)_2(CH_2SiMe_3)_2(PMe_3)_2$ when the reaction stoichiometry MgR_2 : $Mo_2(O_2CMe)_4$ = 2 : 1 is used. The i.r. and n.m.r. data are consistent with the structure (II) determined by an X-ray diffraction study.[19] The acetates are bridging and the phosphine groups are trans to each other with respect to the Mo-Mo quadruple bond.

Using an excess of $Mg(CH_2SiMe_3)_2$ leads to a very air-sensitive, red, crystalline compound of apparent stoichiometry $Mo_2(CH_2SiMe_3)_3(PMe_3)_3$ (1.C). This compound is also obtained when (1.B) is treated with excess $Mg(CH_2SiMe_3)_2$ and PMe_3. While much information can be obtained from n.m.r. data, the assignments (Tables 1.2, 1.3) have been made on the basis of the structure (III) as determined by X-ray diffraction.[19] A similar complex of trimethylphosphite, $Mo_2(CH_2SiMe_3)_2((CH_2)_2SiMe_2)[P(OMe)_3]_3$ (1.G) has also been isolated. The structure (III) has two molybdenum atoms, linked by a strong metal-metal bond (2.16 Å), bridged by one $(CH_2)_2SiMe_2$ group forming a novel five-membered heterocycle. Three PMe_3 groups are bonded to one molybdenum atom while two normal $-CH_2SiMe_3$ groups are attached to the other.

The ^1H n.m.r. spectrum is deceptively simple consisting of a multiplet (area 27) due to the PMe_3 groups and two singlets (δ 0.84, 0.28) (areas approx. 8 : 18). Peaks due to the various methylene protons are not observed although integration of the spectrum indicates



(II)



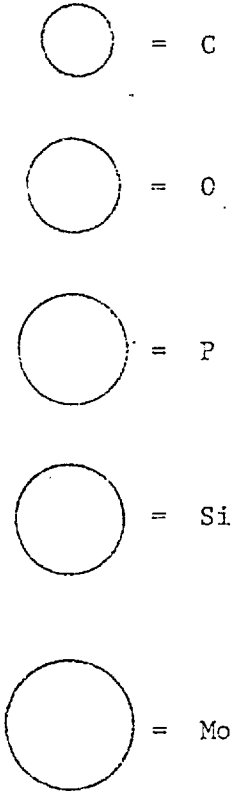
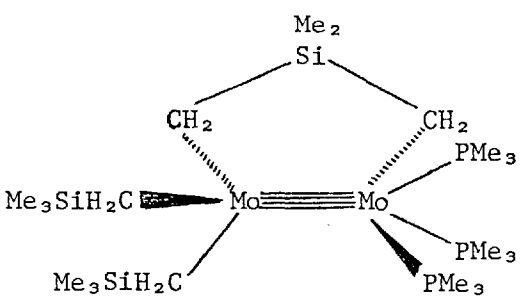


Figure (II) X-ray Crystal Structure of $Mo_2(O_2CMe)_2(PMe_3)_2(CH_2SiMe_3)_2$ (1.B)



(III)

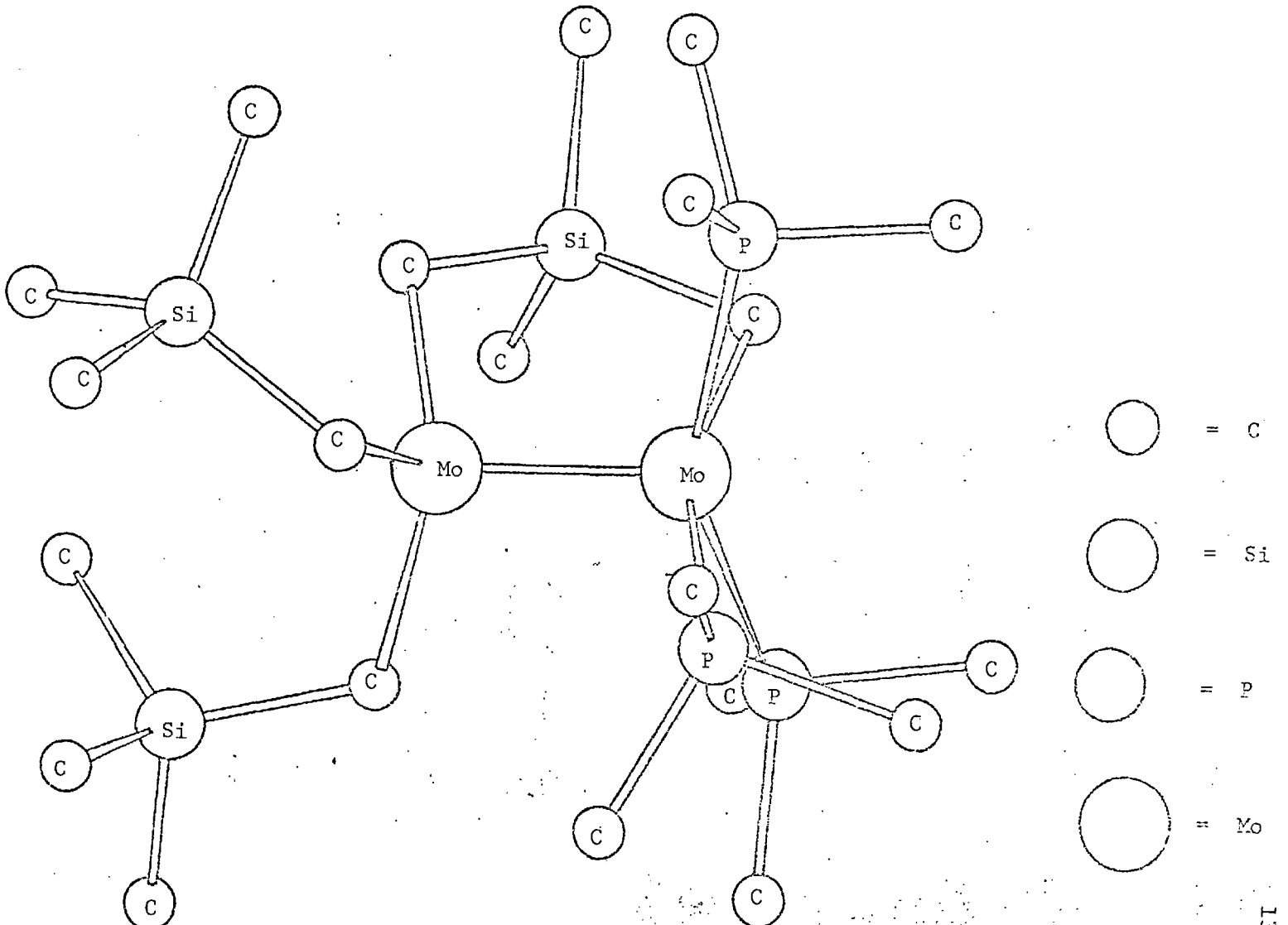


Figure (III) X-ray Crystal Structure of $Mo_2((CH_2)_2SiMe_2)(CH_2SiMe_3)_2(PMe_3)_3$ (1.C)

that they are probably masked by either of the two SiMe resonances.

The AX_2 triplet-doublet pattern of the $^{31}P\{H\}$ n.m.r. confirms the presence of three phosphine groups attached to one molybdenum atom in solution as in the crystalline state. Two are trans and equivalent while the third is cis to both of them.

The methylene carbon atoms of the bridging $(\underline{C}H_2)_2SiMe_2$ unit should give two separate peaks in the $^{13}C\{H\}$ n.m.r. spectrum. However only one slightly broadened peak (δ 73.62) which can be assigned to these atoms is observed.

The bridging $(CH_2)_2SiMe_2$ group is no doubt formed by the elimination of a γ-hydrogen from a $MoCH_2SiMe_3$ group. A similar process probably occurs in the formation of the four-membered heterocycles (1.I) and (1.L) obtained from $Ru_2(O_2CMe)_4C\ell$ and $Rh_2(O_2CMe)_4$ respectively.[15] However the methylene unit which is generated in this case becomes attached to the other molybdenum atom. There is no obvious explanation for the unsymmetrical structure of this alkyl which formally has Mo^{I} and Mo^{III} atoms.

Neopentyl. The neopentyl analogue of (1.B), namely $Mo_2(CH_2CMe_3)_2(O_2CMe)_2(PMe_3)_2$ (1.D) is readily obtained and spectroscopic data for the red air-sensitive compound indicate that it has a structure similar to (II) with acetato bridges.

When a large excess of alkylating agent was used a deep green air--sensitive and petroleum-soluble substance was obtained. However it was not possible to obtain pure samples of this oily material. There is no acetate present according to n.m.r. spectra.

CHAPTER 2

ARYLS OF Mo(II), Re(III), Ru(II) AND Rh(I)

I. INTRODUCTION

The interaction between diarylmagnesiums, $MgAr_2$, Ar = C_6H_5, 2-$MeOC_6H_4$ and 4-FC_6H_4, and the metal-metal bonded binuclear bridged tetracetates, $M_2^{II}(CO_2Me)_4$, M = Mo, Rh, and $Ru^{II,III}(CO_2Me)_4C\ell$ in the presence of trimethylphosphine produces monomeric (Ru, Rh) or dimeric (Mo) aryls; for Ru and the 2-methoxyphenyl, hydrogen loss from the MeO group leads to formation of a metallocycle. In the absence of PMe_3, $Re_2(CO_2Me)_4C\ell_2$ gives a dimeric binary aryl, $Re_2(2\text{-}MeOC_6H_4)_6$.

Analytical (Table 2.1) and n.m.r. spectroscopic data (Tables 2.2 and 2.3) are in the Experimental Section.

II. RESULTS AND DISCUSSION

1. Molybdenum Compounds

(a) Phenyl and 4-fluorophenyl. The interaction of μ_4-tetraacetatodimolybdenum(II) (Mo-Mo), $Mo_2(CO_2Me)_4$, with the diarylmagnesium in diethyl ether containing excess PMe_3 produces blue solutions from which dark blue diamagnetic crystals of stoichiometry $Mo_2(CO_2Me)Ar_3(PMe_3)_3$, Ar = Ph (2.A), 4-$FC_6H_4$ (2.B), can be isolated in high yield. In the absence of phosphine only decomposition occurs. Analytical and spectroscopic data are consistent with the structure (IVa, IVb) in which the molybdenum is in the divalent state with a quadruple Mo-Mo bond. The presence of a μ-acetato group is shown by ^1H and ^{13}C n.m.r. spectra although in the i.r., identification of carboxylate stretches is uncertain

due to obscuring absorptions of aryl and phosphine groups. Since there are only weak aryl absorptions above ca. 1520 cm^{-1} it is evident that the CO_2Me group cannot be unidentate.[21]

Deuteration experiments (see Experimental) show that all three aryl groups are σ-bonded. While the ^1H and ^{13}C n.m.r. data is not rigorously diagnostic of structure, the $^{31}P\{^1H\}$ spectra consists of AB_2 and AMX type resonances, which clearly indicates the existence in solution of two isomers. On warming, the resonances coalesce giving two broad bands at 50° C and a singlet at ca. 75° C. Corresponding behaviour is found in the ^1H n.m.r. spectra. On cooling the original spectra are restored which suggests that rapid PMe_3 exchange occurs at elevated temperatures but is sufficiently slow at 35° C for both isomers to be observed in $^{31}P\{^1H\}$ spectra. Attempts to separate isomers were unsuccessful. The ^1H spectra of both phenyl and fluorophenyl show two singlets due to acetate at 35° which coalesce to a singlet at 70° where the phosphines are equivalent and again the spectra indicate isomers. Taken together the n.m.r. data is consistent with (IVa), AB_2, and (IVb), AMX. An AB_2 pattern should be obtained from an isomer with the aryl on Mo_1 in the axial position with respect to the Mo-Mo bond. However, as the CO_2Me group gives two CH_3 resonances in both phenyl and fluorophenyl compounds it seems reasonable to assume that the group trans to oxygen on Mo_1 is an aryl for isomer (IVa) and a PMe_3 for the other (IVb), (see page 22).

The spectra do not rigorously exclude a structure with three PMe_3 groups on one Mo atom and three aryls on the other but the unusual $^{31}P\{^1H\}$ spectra are inconsistent with this.

(b) 2-Methoxyphenyl. The reaction in this case yields $Mo_2(2\text{-}MeOC_6H_4)_4(PMe_3)_2$ (2.C). The dark blue-green crystalline and air

stable compound contains no acetate and the $^{31}P\{^{1}H\}$ spectrum is a singlet (+35° to -40° C) consistent with the structure (V) having PMe_3 groups on the Mo≡Mo bond axis. The aryl groups act like bridging bidentate carboxylate groups being formally 3-electron donors *via* carbon and the methoxy oxygen. Increased stability with this type of chelate aryl is well known [1] and the bonding is doubtless similar to that of the 2,6-dimethoxyphenyl ligand in $Cr_2(2,6\text{-}(MeO)_2C_6H_3)_4$.[22] The spectroscopic data tells nothing of the relative orientations of the aryls and (V) shows only one possibility with mutually *cis* units.

The compound is unstable in organic solvents at room temperature - the solutions turning grey-green and depositing a pink precipitate. Cryoscopic molecular weight determinations (benzene) on fresh solutions give values *ca.* half the expected due to PMe_3 dissociation, which is also indicated by ^{1}H and $^{31}P\{^{1}H\}$ spectra on other than fresh solutions.

The pink precipitate, which is exceedingly pyrophoric when dry, is $Mo_2(2\text{-}MeOC_6H_4)_4$ (2.D). It is soluble in $CH_2C\ell_2$ and Me_2SO, being sufficiently stable in the latter to allow ^{1}H n.m.r. and molecular weight studies and presumably it has a structure similar to (V) without the terminal phosphines.

Direct interaction of $Mo_2(CO_2Me)_4$ and $(2\text{-}MeOC_6H_4)_2Mg$ in absence of PMe_3 in ether also gave a pink product. However it proved impossible to separate it cleanly from magnesium acetate. Chromium(II) acetate gives a bright yellow compound with properties similar to those of $Cr_2(2\text{-}MeOC_6H_4)_4$ [23] but reproducible analytical data could not be obtained.

2. Rhenium Compounds

In the absence of PMe_3, the acetate $Re_2(CO_2Me)_4C\ell_2$ reacts with

three equivalents of di-2-methoxyphenyl magnesium to give dark green solutions from which the dark green, diamagnetic, crystalline rhenium(III) aryl of formula $Re_2(2\text{-}MeOC_6H_4)_6$ (2.E), can be isolated in high yield. Although sparingly soluble in hydrocarbons it is quite soluble in acetone and chlorinated solvents.

The ^1H n.m.r. spectrum at 25° C has aryl resonances and a singlet due to $C\underline{H}_3O$. This broadens at 0° C and at -20° becomes two singlets (ratio 2 : 1, separation ca. 7 Hz). The $^{13}C\{^1H\}$ spectrum at 25° C shows two broadened resonances for $C\underline{H}_3O$ (ca. 2 : 1).

The spectra suggest that there are aryl groups in two environments as in (VI). The terminal aryls are not necessarily chelate as shown and the singlet $C\underline{H}_3O$ (25° C) suggests exchange between end and bridge positions, presumably by simple lift-off of the methoxy oxygen. However, the $^{13}C\{^1H\}$ spectrum still permits two different $C\underline{H}_3O$ groups to be detected at 25°. The separation between these peaks is ca. 36 Hz so the coalescence temperature for the ^{13}C will be higher than that for the ^1H spectrum.

Interaction of $Re_2(CO_2Me)_4C\ell_2$ and $MgAr_2$ in the presence of PMe_3 yield red-brown materials from which no pure compounds could be isolated. Using $MgPh_2$ and $Mg(C_6H_4F)_2$ alone, petroleum soluble, brown but intractable products were also obtained.

3. Ruthenium Compounds

(a) Phenyl. The acetate $Ru_2(CO_2Me)_4C\ell$ reacts with Ph_2Mg in tetrahydrofuran containing PMe_3 to give the complex $RuPh_2(PMe_3)_4$ (2.F). This off-white, crystalline, diamagnetic compound is surprisingly air-sensitive and traces of moisture or oxygen cause rapid decomposition.

The ^1H resonance of $C\underline{H}_3$-P (25° C) is a slightly broadened singlet which broadens further on cooling. The $^{31}P\{^1H\}$ spectrum is also a

singlet at room temperature but at -40° C in diethyl ether under dinitrogen has an $\underline{A_2X_2}$ triplet-triplet pattern consistent with a structure with cis phenyl groups in cis-$RuPh_2(PMe_3)_4$ together with an $\underline{AX_2}$, triplet doublet pattern and a free $\underline{P}Me_3$ (δ -62.9 [24]) resonance line, suggesting the presence of a species with three phosphines per Ru. Since the i.r. spectra of Nujol mulls or solutions under N_2 have a strong sharp band at 2128 cm^{-1} that disappears on sweeping with argon it is evident that in solution there are equilibria

$$\underline{cis}\text{-}RuPh_2(PMe_3)_4 \rightleftharpoons RuPh_2(PMe_3)_3 + PMe_3$$

$$RuPh_2(PMe_3)_3 + N_2 \rightleftharpoons RuPh_2(N_2)(PMe_3)_3$$

There is no nitrogen analytically in the solid and since the molecular weight under argon is only slightly low for $RuPh_2(PMe_3)_4$ the dissociation appears not to be extensive.

A reversible colour change is observed on heating the compound in solution. At room temperature solutions are pale yellow while at ca. 50° C they become orange. The compound reacts with CO, NO and alkenes although the products have not yet been fully investigated. No reaction took place after heating in a sealed tube for one week at 200° C in neat PMe_3 or after u.v. irradiation (48 h) at room temperature in benzene or PMe_3.

(b) 2-Methoxyphenyl. The reaction of 2.5 equivalents of the diarylmagnesium with $Ru_2(CO_2Me)_4Cl$ and PMe_3 in tetrahydrofuran at 25° is slow (12 hours). The yellow solution produced contains a mixture of species, including, according to ^{31}P n.m.r. a bridged phosphido complex. It was found impossible to separate the components by crystallisation. On chromatography after elution with tetrahydrofuran a white complex $Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4$ (2.G) can be isolated. Spectroscopic data

indicates a structure (VII) confirmation of which is provided by X-ray crystallographic study.[19] The compound can be considered to arise by oxidative addition of a C-H bond of the methyl group across ruthenium followed by loss of H to give a Ru-CH_2- bond in a five-membered Ru^{II} heterocycle. The δ-elimination has a precedent in the formation of the heterocycle $Ru[(CH_2)_2SiMe_2](PMe_3)_4$.[15]

The ^1H n.m.r. spectrum shows methylene -$C\underline{H}_2$- protons giving a well defined first order pattern of a 1 : 2 : 1 triplet ($^3J_{P-H}$ = 15 Hz) of doublets of doublets ($^3J_{P-H}$ = 5 Hz and 2 Hz respectively). The triplet structure can be ascribed to splitting by the two mutually trans PMe_3 groups and the doublet of doublets from the two cis, non-equivalent PMe_3 groups. The cis P coupling with $C\underline{H}_2$ thus is apparently greater than trans-P coupling.

The $^{31}P\{^1H\}$ n.m.r. in benzene (10% C_6D_6) is consistent with (VII) and has two triplets of doublets due to the cis-non-equivalent phosphines (see Table 2.3). The two trans equivalent phosphines give a doublet of doublets ($^2J_{P_A-P_B}$ = 25.2 Hz, $^2J_{P_A-P_C}$ = 27.9 Hz) as coupling to each of the mutually cis phosphines is slightly different.

4. Rhodium Compounds

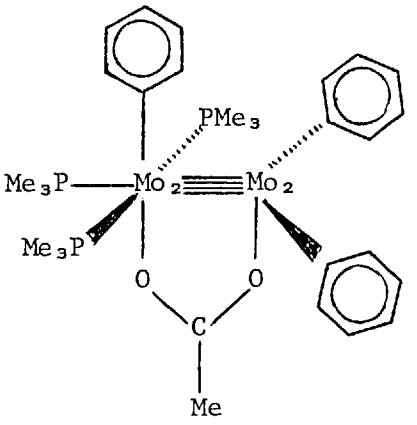
(a) Phenyl. Interaction of $Rh_2(CO_2Me)_4$, Ph_2Mg and PMe_3 in diethyl ether produces the orange, crystalline compound $RhPh(PMe_3)_3$ (2.H), in high yield. Unlike the triphenylphosphine analogue,[25] the compound is readily obtained pure and decomposes only slowly in air.

N.m.r. spectra are temperature dependent. The $C\underline{H}_3$-P singlet at room temperature becomes a broad doublet and a singlet at -20° and below. The $^{31}P\{^1H\}$ spectrum has a distorted doublet ($^1J_{Rh-P}$ = 142.1 Hz) at room temperature and a pattern of at least 12 lines at -40°. The data does not permit a structural assignment though as is usual with Rh^I

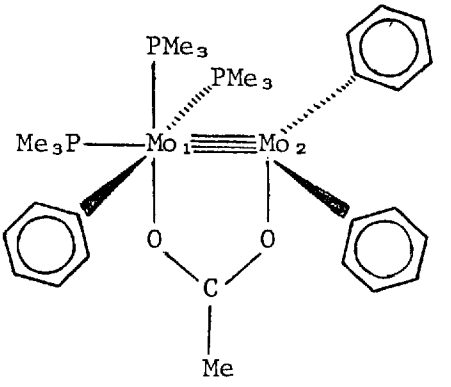
compounds a distorted square structure seems likely, possibly with solvent coordination in solution giving a fluxional 5-coordinate species.

(b) 2-Methoxyphenyl. The isolated yellow crystals of $Rh(2\text{-}MeOC_6H_4)(PMe_3)_3$ (2.I), are thermally more stable and less air sensitive than the phenyl, probably due to coordination of oxygen as in (VIII). The n.m.r. spectra are again temperature dependent, and complicated and a detailed analysis was not attempted. At 25° there is a ^1H singlet, and a $^{31}P\{^1H\}$ doublet with $^1J_{Rh-P}$ = 146.2 Hz.

In the absence of PMe_3 petroleum soluble, red-brown but intractable products were obtained for both phenyl and 2-methoxyphenyl.



(a)



(b)

Figure (IV) $Mo_2(O_2CMe)Ar_3(PMe_3)_3$, (2.A, 2.B)

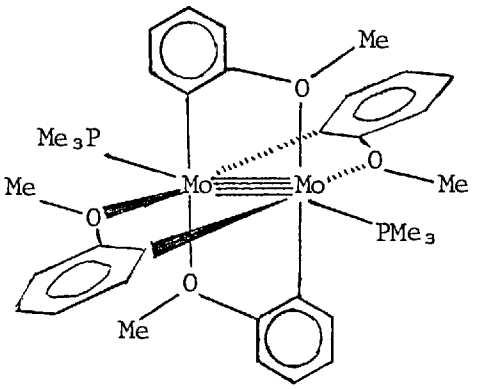


Figure (V)

$Mo_2(2\text{-}MeOC_6H_4)_4(PMe_3)_2$ (2.C)

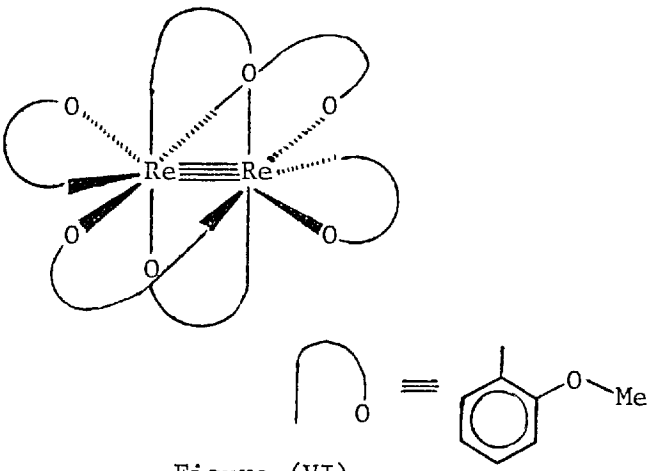


Figure (VI)

$Re_2(2\text{-}MeOC_6H_4)_6$ (2.E)

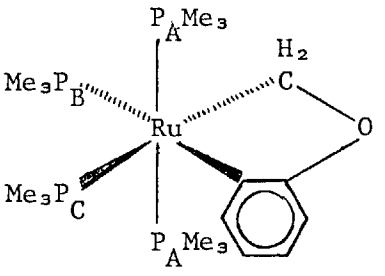


Figure (VII)

$Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4$ (2.G)

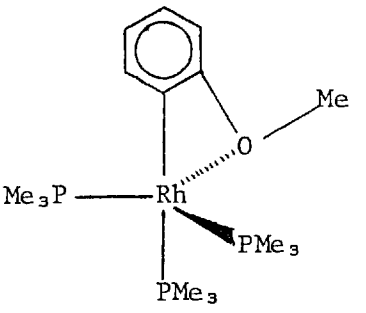


Figure (VIII)

$Rh(2\text{-}MeOC_6H_4)(PMe_3)_3$ (2.I)

CHAPTER 3

DIMERIC RHENIUM(III) ALKYLS

I. INTRODUCTION

Many rhenium alkyls are known [26] but previously none had acetates bridging quadruply bonded metal-metal units. In the absence of PMe_3 neutral, acetate bridged, binuclear alkyls of stoichiometry $Re_2R_4(O_2CMe)_2$, (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph, and CH_2Ph) are obtained from the interaction of the dialkyl magnesiums, R_2Mg, with tetraacetato-dichlorodirhenium(III), $Re_2(O_2CMe)_4Cl_2$, in diethyl ether.

A binuclear methyl compound $Re_2Me_2(O_2CMe)_4$ is obtained from the interaction of dilithium octamethyldirhenate(III), $Li_2Re_2Me_8.2Et_2O$, with acetic acid, and several derivatives containing the "$Re_2Me_2(O_2CMe)_2$" unit are also described. Analytical (Table 3.1) and spectroscopic data (Table 3.2) are in the Experimental Section.

II. RESULTS AND DISCUSSION

1. Methyl Compounds

(a) Bis(acetato methyl)bis-μ-acetatodirhenium(III) (Re-Re) This bright red, air stable, crystalline compound (3.A), can be isolated in ca. 50% yield from the interaction of solid $Li_2Re_2Me_8.2Et_2O$ and excess acetic acid. The structure (IX) has recently been determined by X-ray diffraction;[19] two acetate groups bridge two rhenium atoms linked by a short metal-metal bond while each metal holds an unsymmetrical chelate acetate and a methyl group. The latter are trans to each other with respect to the Re-Re axis and each rhenium atom has a roughly octahedral

environment. A structure of this type has not been previously reported for binuclear multiply bonded transition metal acetates.[27] The bond distances suggest that the Re-CH_3 groups are strongly bound while the oxygen atoms of the chelating acetates occupying the coordination sites along the Re-Re axis are weakly bound.[19] The i.r. spectrum contains a strong absorption at 1555 cm^{-1} (ν_{CO}) which is probably due to the asymmetric bidentate acetate group. This band is not found in the spectra of derivatives of (3.A) which appear to contain only the symmetrical bridging acetates and these have lower C-O stretching frequencies. The ^1H n.m.r. spectrum consists of three equal peaks indicating that the structure in solution is similar to that in the solid state.

(b) Other Methyl Compounds. In dichloromethane (3.A) reacts with chlorine gas to give a purple powder of stoichiometry $\{ReMe(O_2CMe)C\ell\}_n$, (3.B). The compound is insoluble in most solvents although red, air stable crystals of stoichiometry $Re_2Me_2(O_2CMe)_2C\ell_2(Me_2)SO$ (3.C) can be obtained from dimethylsulphoxide. The structure of (3.B) is probably polymeric - with chlorine atoms bridging the $[Re_2Me_2(O_2CMe)_2]$ units (X) since the X-ray crystal structure of (3.C) [19] shows that this retains the " $Re_2(O_2CMe)_2Me_2$" unit with the methyl groups trans with respect to Re-Re (XI). One molecule of dimethyl sulphoxide is bound to one end of the molecule via its oxygen atom [28] (i.r., ν_{SO} = 935 cm^{-1}) while no corresponding ligand is found at the other end of the molecule. The basic structure is quite similar to those of the binuclear mixed halo-acetates of rhenium(III).[29]

Compounds of formula $Li_2Re_2Me_{(8-x)}C\ell_x$ are probably formed when insufficient methyllithium is used in the preparation of $Li_2Re_2Me_8.2Et_2O$. The action of glacial acetic acid on these solutions (see Experimental)

results in the formation of an insoluble purple material which still retains chlorine. Microanalytical data was not reproduceable and we have been unable to purify it by other means. However, with dimethylsulphoxide this material yields red crystals of (3.C). The mixed methyl-chloro species which are produced are probably similar to those of tungsten in $Li_4W_2(Me)_{8-x}C\ell_x.4thf$.[30]

On warming (3.A) in methanol a mauve insoluble powder of stoichiometry $\{ReMe(OMe)(O_2CMe)\}_n$ (3.D) is formed. The i.r. spectrum (ν_{CO}, 1025 cm^{-1}) indicates the presence of a methoxide.[31] The structure might be similar to that of (3.B) but with methoxide bridges [32] instead of chlorine bridges.

2. Tetraalkyl(μ-bisacetato)dirhenium(III) Compounds

Trimethylsilylmethyl and Neopentyl Deep red, air stable crystals of $Re_2R_4(O_2CMe)_2$, ($R = CH_2SiMe_3$, CH_2CMe_3), (3.E), (3.F), are obtained in high yield from the interaction of $Re_2(O_2CMe)_4C\ell_2$ and the corresponding dialkylmagnesium in diethyl ether. The compounds are isostructural (XII) on the basis of n.m.r. and molecular weight data. Two rhenium atoms, retaining the metal-metal bond, are bridged by two acetate units and two alkyl groups are bonded to each rhenium(III) atom. The ^1H n.m.r. spectra consist of three singlets (relative areas 3 : 4 : 18) indicating that all four alkyl groups are equivalent.

The use of a large excess of the magnesium dialkyl merely results in the more rapid formation of (3.E) or (3.F).

The compounds are quite soluble in dichloromethane, methanol and acetone as well as hydrocarbon solvents, without decomposition for several weeks. They do not react with H_2, CO, or C_2H_4 under ambient conditions (1 atm., room temperature). With NO, in petroleum, red brown solutions are obtained although no pure compounds could be isolated.

Neophyl The neophyl analogue of (3.E) and (3.F), $Re_2(CH_2CMe_2Ph)_4(O_2CMe)_2$, (3.G), is insoluble in petroleum and only moderately soluble in benzene. However it is quite soluble in chloroform and can be recrystallised from dichloromethane as red prisms. N.m.r. data (Table 3.2) show that it is isostructural with (3.E) and (3.F) although it survives in air only for days instead of weeks.

Benzyl The benzyl compound, $Re_2(CH_2Ph)_4(O_2CMe)_2$ (3.H), is formed quite rapidly (ca. 15 min) in high yield under similar conditions to those described above for the other alkyls. It can only be handled briefly in air and is insoluble in hydrocarbon solvents. However, it may be obtained as purple crystals from diethyl ether and survives sufficiently long enough in $CDC\ell_3$ for n.m.r. data to be obtained.

Molecular weight measurements were not made due to its insolubility in hydrocarbons and air sensitivity, though the n.m.r. data suggests that it is isostructural with (3.E), (3.F), and (3.G).

The interaction of $Re_2(O_2CMe)_4C\ell_2$ and the dialkyl magnesiums in the presence of excess PMe_3 results in low yields of materials and no attempts to characterize them fully were made.

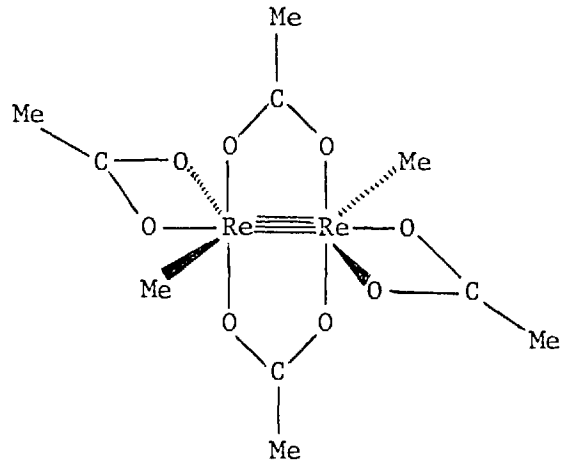


Figure (IX)

$Re_2Me_2(O_2CMe)_4$ (3.A)

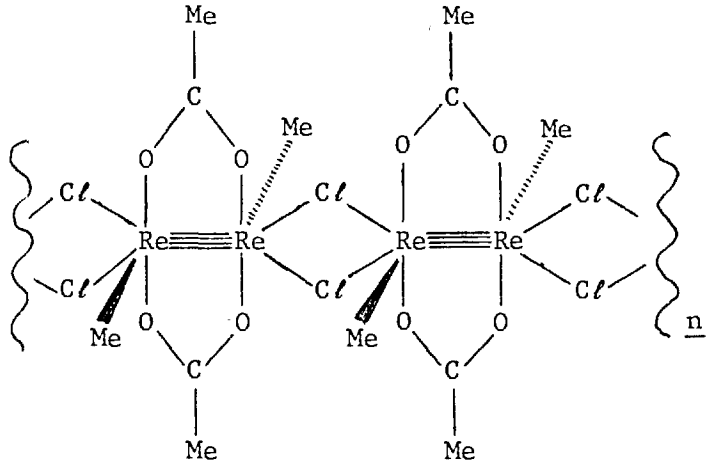


Figure (X)

$\{ReMe(O_2CMe)C\ell\}_n$ (3.B)

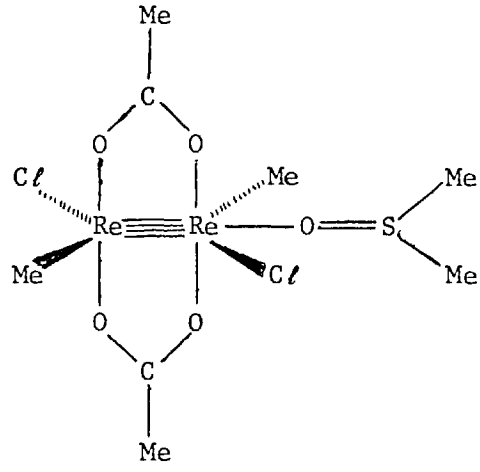
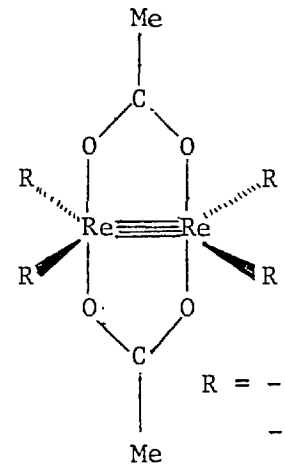


Figure (XI)

$Re_2Me_2(O_2CMe)_2C\ell_2Me_2SO$ (3.C)



R = $-CH_2SiMe_3$
$-CH_2CMe_3$
$-CH_2CMe_2Ph$
$-CH_2Ph$

Figure (XII)

$Re_2R_4(O_2CMe)_2$ (3.E-3.H)

CHAPTER 4

RUTHENIUM(III) METHYLENE BRIDGED COMPOUNDS

I. INTRODUCTION

Compounds containing a single bridging $-CH_2-$(methylene) unit have been reported only for manganese,[33] rhodium,[34] osmium,[35] and platinum.[36] A terminal methylene carbene complex has also been isolated.[37] Bridging carbenes in which groups other than hydrogen are attached to the bridge carbon are also known for manganese,[33, 38] rhenium,[39] iron,[40] cobalt,[41] rhodium,[34, 42] and platinum.[36]

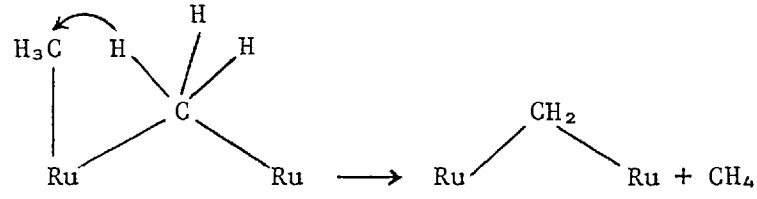
The interaction of dimethylmagnesium with the ruthenium(III) trinuclear-μ_3-oxo centered acetate, $[Ru_3O(O_2CMe)_6(H_2O)_3](O_2CMe)$ in the presence of trimethylphosphine yields a unique complex of stoichiometry $(Me_3P)_3Ru(\mu\text{-}CH_2)_3Ru(PMe_3)_3$ (4.A), containing three bridging methylene groups. The interaction of this complex with one equivalent of fluoroboric acid yields a +1 cationic species $[(Me_3P)_3Ru(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)Ru(PMe_3)_3]\text{-}BF_4$ (4.B), in which one methylene is protonated to give a bridging methyl group. With two equivalents of acid (HBF_4 or HSO_2CF_3) +2 cationic complexes $[(Me_3P)_3Ru(\mu\text{-}CH_2)_2Ru(PMe_3)_3](X)_2$ (X = BF_4, (4.C); X = SO_3CF_3 (4.D)) are formed with loss of methane; these contain only two bridging methylene groups.

The compounds have been studied by ^1H, ^{31}P and ^{13}C n.m.r. spectroscopy and their structures have been determined by X-ray crystallography.[42,44] Analytical data is presented in Table 4.1 and n.m.r. data in Tables 4.2 and 4.3.

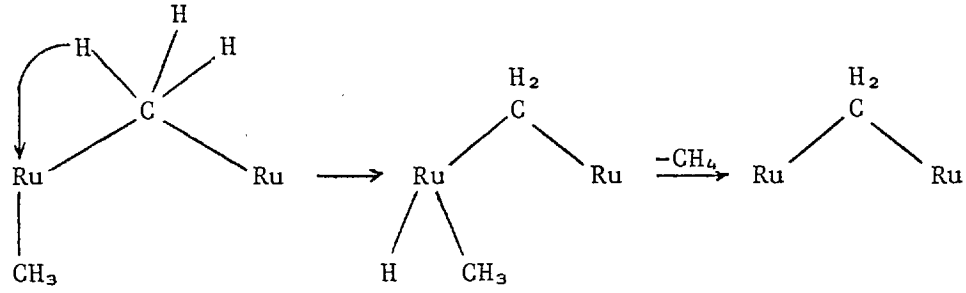
II. RESULTS AND DISCUSSION

1. Hexakis(trimethylphosphine)tris-μ-methylenediruthenium(III)(Ru-Ru) (4.A)

This diamagnetic, moderately air sensitive, orange-red crystalline compound was originally isolated in low yield from the reaction between Me_2Mg and $Ru_2^{II,III}(O_2CMe)_4Cl$ in the presence of excess PMe_3; the main product in this reaction is cis-$RuMe_2(PMe_3)_4$.[15,43] Much higher yields of (4.A) are obtained if the trinuclear-μ_3-oxocentered ruthenium(III) acetate $[Ru_3O(O_2CMe)_6(H_2O)_3](O_2CMe)$ [44] is used. The identity of the compound (4.A) was determined by a single crystal X-ray study [44] and the structure of the molecule is shown in Figure XIII. The mechanism of formation of (4.A) from the oxo-centered ruthenium(III) trimer is obscure but it seems reasonable to suppose that some type of α-hydrogen transfer from intermediate methyl species is involved, e.g.,



or, less likely, since it would require an oxidative addition to a ruthenium atom already in a +2 or +3 state,



Similar hydrogen transfers have been reported in triosmium carbonyl cluster compounds.[35]

The overall coordination geometry is approximately a confacial

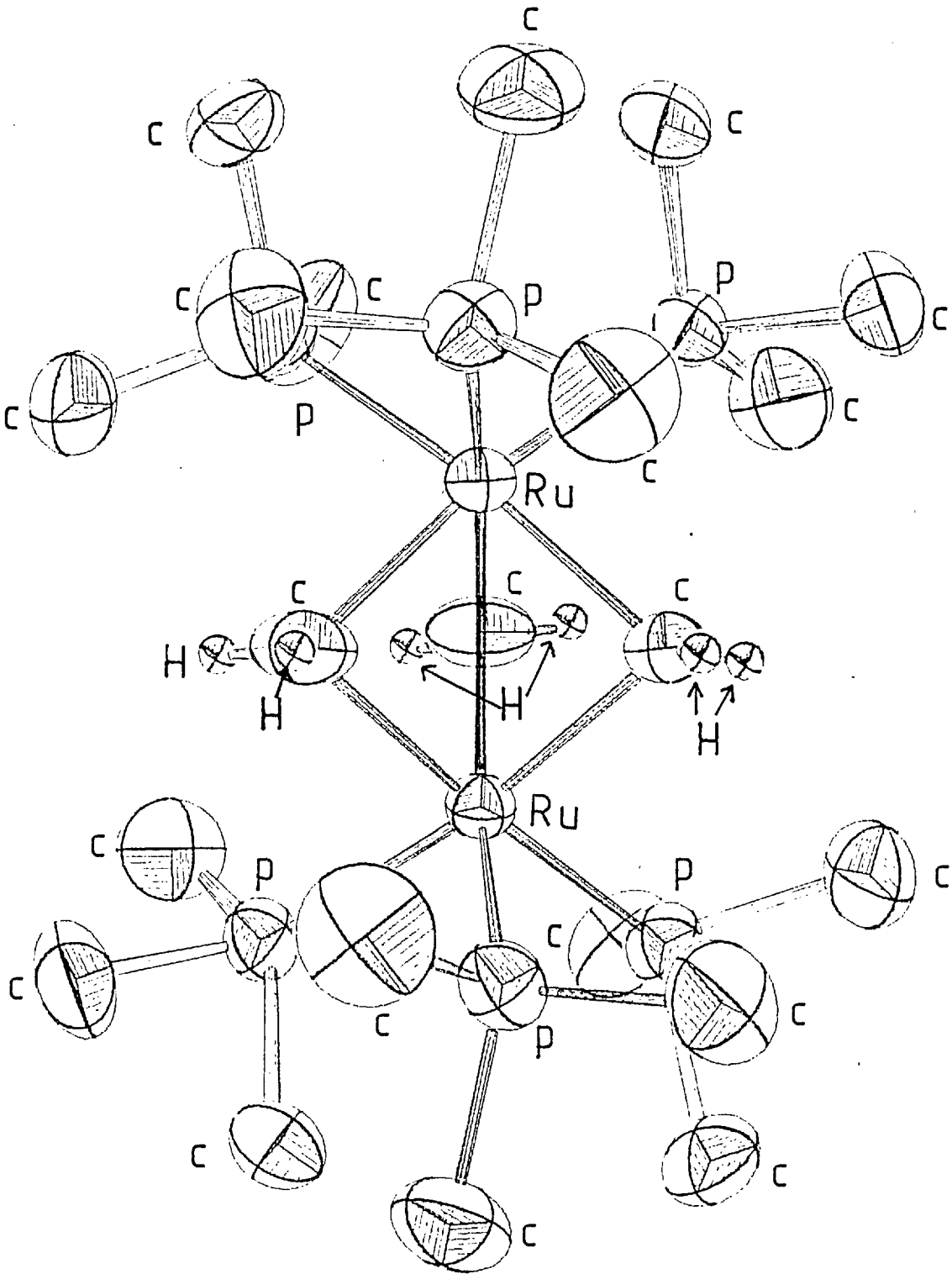


Figure XIII. $(Me_3P)_3Ru(CH_2)_2Ru(PMe_3)_3$ X-ray Structure. (4.A)

bioctahedron and is similar to that in $[Ru_2Cl_3(PPhEt_2)_6]^+$,[46] $Ru_2Cl_4(PPhEt_2)_5$,[47] and $Ru_2Cl_5(PBu^n_3)_4$,[48] all of which contain three bridging chlorine atoms. The short Ru-Ru distance (2.650(1) Å) is short and suggests the presence of a single bond between the two Ru atoms as required by the observed diamagnetism of the compound.

N.m.r. data is consistent with the X-ray diffraction study. The ^1H and $^{13}C\{^1H\}$ resonances for the sp^3 hybridized methylene groups are shifted well downfield, as observed for the other well characterised bridging $-CH_2-$ compounds,[33,34] although not as far as in $(\eta-C_5H_5)_2Ta(CH_3)(CH_2)$.[37] The signals have a triplet structure due to coupling to phosphorus (^1H, δ 5.22, broad triplet, J = 15 Hz; $^{13}C\{^1H\}$, δ 131.26, triplet of triplets, J = 45.4, 5.1 Hz). The trimethylphosphine resonances also have a triplet structure (^1H, δ 1.42, J = 5.0 Hz; $^{13}C\{^1H\}$, δ 24.4, J = 7.1 Hz), while the $^{31}P\{^1H\}$ spectrum is a sharp singlet confirming the equivalence of the phosphine groups.

2. Hexakis(trimethylphosphine)bis-μ-methylene-μ-methyldiruthenium(III) tetrafluoroborate (4.B)

The interaction of (4.A) with one equivalent of fluoroboric acid in tetrahydrofuran yields a diamagnetic, air stable, dark red crystalline compound (4.B). Analytical and conductivity data indicate that this compound is a 1 : 1 tetrafluoroborate salt. N.m.r. spectra show that one of the bridging methylene units in (4.A) has been protonated to give a bridging methyl ($-CH_3$) group. Although rare, other examples of methyl groups bridging transition metals have been reported.[35,49,50]

In the ^1H n.m.r. spectrum of (4.B), the resonance assigned to the bridging methyl group is shifted greatly upfield (δ -5.65, area 3). The coupling to phosphorus gives a symmetrical pentuplet ($^3J_{^{31}P-^1H}$ = 2 Hz). Although this resonance is in the region generally considered to be

characteristic of transition metal M-H bonds there is no evidence for Ru-H bonds from i.r. spectra in the solid state or in solution. A high upfield shift (δ -3.68) was also reported for the bridging methyl group in $HOs_3(CO)_{10}(CH_3)$ [3] although the bridge methyls of $Re_3(CH_3)_9(C_5H_5N)_3$ [49] resonated in the normal region at δ -0.7. The H atoms of the two remaining methylene bridges resonate downfield from the $-CH_2-$ signals in the neutral complex, at δ 7.07, as a slightly distorted quartet ($^3J_{^{31}P-^1H}$ = 6 Hz). In the $^{13}C\{^1H\}$ n.m.r. spectrum the broad resonance to high field of Me_4Si can be assigned to the bridging methyl group (δ -27.1) and again large upfield shifts occur for $HOs_3(CO)_{10}(CH_3)$ [35] (δ -59.2) and $Re_3Me_9(PEt_2Ph)_3$ (δ -11.83).[51] The methylene carbon atoms give a single slightly broadened resonance, shifted well downfield as in (4.A) (δ 147.6) At -80° C the resonances are much broader. The $^{31}P\{^1H\}$ n.m.r. spectrum consists of a single, sharp resonance at 65° C which becomes very broad at room temperature and at -80° C two considerably sharper resonances are observed (relative intensity 1 : 2). This low temperature spectrum accords with the crystal structure in the solid state where there are two equivalent and one unique phosphorus atoms. At elevated temperatures some type of fluxional behaviour is evidently occurring. The ^1H n.m.r. resonances also broaden on cooling and are slightly sharper at +50° C.

The crystal structure of (4.B) from X-ray methods is consistent with the formulation derived from the n.m.r. studies [45] (Figure XIV)

3. Hexakis(trimethylphosphine)bis(μ-methylene)diruthenium(III)(Ru-Ru)bis-tetrafluoroborate (4.C)

The action of two equivalents, or an excess of fluoroboric or trifluoromethane sulphonic acid on the neutral compound (4.A), yields the orange, diamagnetic, crystalline, air stable compounds, $[(PMe_3)_3Ru(CH_2)_2Ru(PMe_3)_3](X)_2$ (X = BF_4, CF_3SO_3, (4.C) and (4.D)). The X-ray crystal

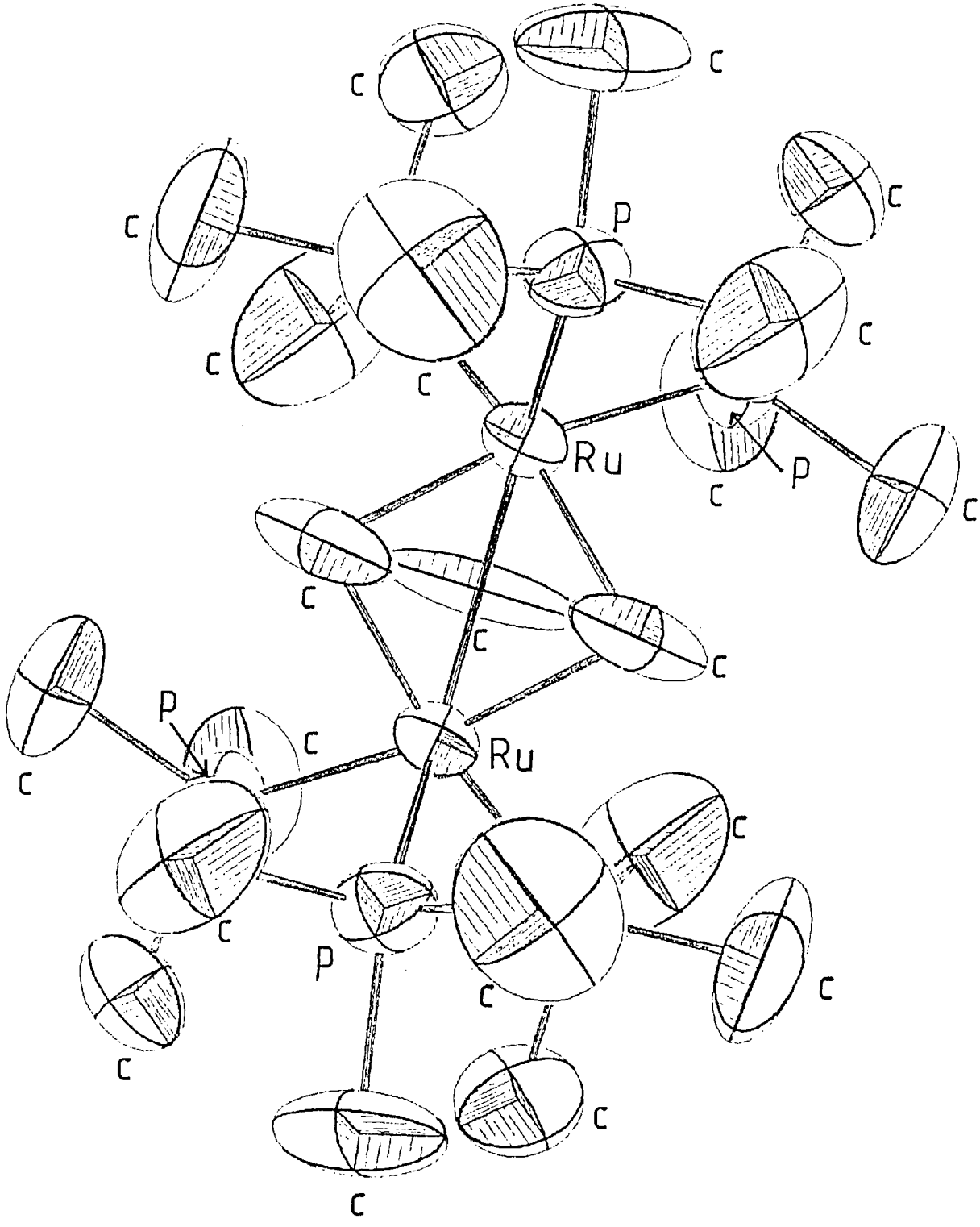
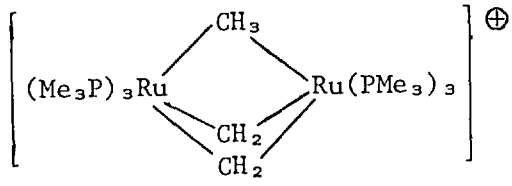
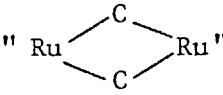


Figure XIV.



(4.B).

X-ray Structure of the Cation.

structure [45] determination of (4.C) revealed the presence of only two bridging methylene groups (Figure XV) giving a planar "  " unit.

The ^{1}H and $^{13}C\{^{1}H\}$ n.m.r. spectra of (4.C) and (4.D) show no high field resonances assignable to a bridging methyl. In the ^{1}H n.m.r. spectrum of (4.C) the bridging methylene groups give a symmetrical pentuplet (δ 8.41, $^{3}J_{^{31}P-^{1}H}$ = 3.5 Hz) at a field lower than observed in either (4.A) or (4.B) - the spectrum of (4.D) is similar. The $^{13}C\{^{1}H\}$ spectrum (4.C) shows a single slightly broadened resonance for the bridging carbon atoms (δ 139.3) and the $^{31}P\{^{1}H\}$ is a single broad peak. The spectra are not temperature dependent. The formation of these compounds doubtless occurs by protonation of a bridging methyl group (as isolated for (4.B)) to give methane, which has been detected by mass spectroscopy.

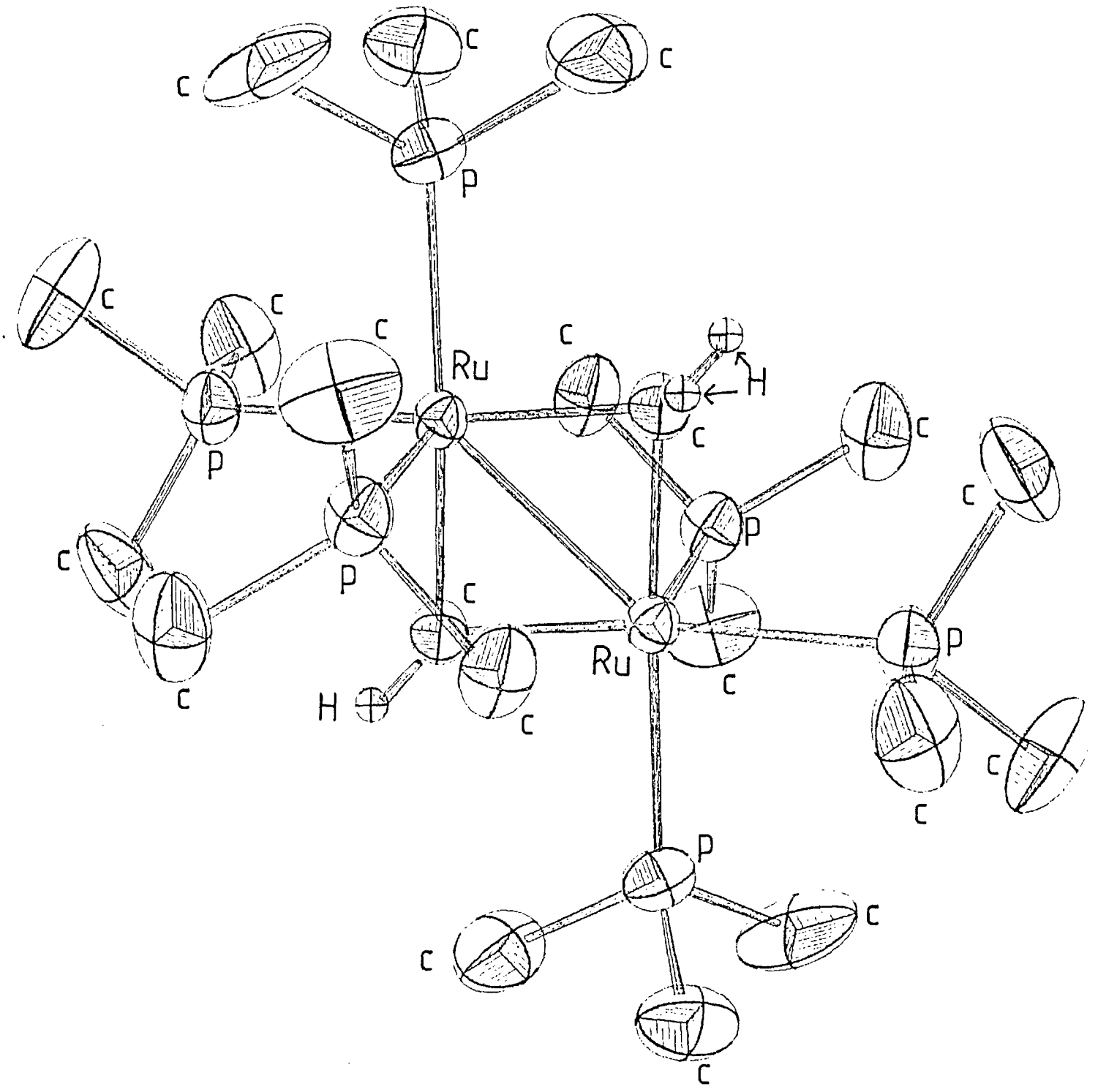


Figure XV. $\left[(Me_3P)_3Ru \begin{matrix} CH_2 \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ CH_2 \end{matrix} Ru(PMe_3)_3 \right]^{2+}$ (4.C).

X-ray Structure of the Cation.

EXPERIMENTAL SECTION

Microanalyses were by the Butterworth Microanalytical Consultancy Limited, Pascher (Bonn) and Imperial College Laboratories. Spectrometers: Perkin-Elmer R12B (^{1}H); Varian XL-100 (^{1}H, ^{13}C, ^{31}P, F.t.); Perkin-Elmer PE 457, 257 (i.r.). All operations were performed under oxygen-free nitrogen or argon or in vacuum and all solvents (except $CH_2C\ell_2$) were dried over sodium and distilled under nitrogen before use. Dichloromethane was dried over calcium hydride and distilled under nitrogen. Petroleum used had b.p. 40-60° C. Melting points were determined in sealed capillaries under nitrogen and are uncorrected.

EXPERIMENTAL CHAPTER 1

The magnetic moment of $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ was determined in solution by Evans' method, the chromium concentration being determined by plasma-arc emission spectroscopy.

(1.A) Bis(trimethylsilylmethyl)bis(μ-trimethylsilylmethyl)bis(trimethylphosphine)dichromium(II) (Cr-Cr)

Bis(trimethylsilylmethyl)magnesium (8.8 cm^3 of a 0.75 M diethyl ether solution) was added to a suspension of $Cr_2(O_2CMe)_4$ (0.56 g, 0.00165 mol) in diethyl ether (40 cm^3) at 0^o C. The mixture was stirred for 5 h at 0^o C. The volatile material was removed under vacuum and the red-brown residue extracted with petroleum (50 cm^3) and filtered. The filtrate was concentrated to ca. 5 cm^3 and cooled (-20^o C) overnight. A white crystalline material was removed from the deep red solution by filtration at 0^o C. Cooling (-20^o C) yielded after ca. 1 week, deep red needles. The compound can also be crystallised from diethyl ether. Yield, 0.3 g, 30%. I.r. (petroleum solution, matched KBr cells), 1276m, 1236s, 1115m, 935s, 865s, 837s, 815s, 735m, 706m, 691m, 672m, 565w, 508w, 458m, 425w. The compound decomposed at ca. 80-100^o C/10^{-2} mm to give a black air-sensitive solid. The compound also decomposes in solution when heated to ca. 50^o C in benzene. Mass spectra show that it does not cleanly eliminate Me_4Si when heated (150^o C) under vacuum.

The compound is soluble in dichloromethane, chloroform and pyridine and survives for several days. It does not react with CO, H_2, ethylene or buta-1,3-diene in petroleum or toluene under ambient conditions. Prolonged treatment with CO (30 min) results in decomposition.

(1.B) Bis-μ-acetatobis[trimethylphosphine(trimethylsilylmethyl)-molybdenum(II)] (Mo-Mo)

Bis(trimethylsilylmethyl)magnesium (1.8 cm^3 of a 0.9 M diethyl ether solution, 0.0016 mol) was added to $Mo_2(O_2CMe)_4$ (0.36 g, 0.00084 mol) suspended in diethyl ether (40 cm^3) and trimethylphosphine (1 cm^3). The red suspension was stirred at 0° C (1 h) and then at room temperature (4 h). The colour of the solution changed from red to deep maroon. After evaporation to dryness the blue residue was dissolved in petroleum ether (30 cm^3), filtered, and concentrated to ca. 10 cm^3. Bright orange-red prisms were obtained after cooling (-20° C). They were washed with cold petroleum (2 x 1 cm^3) and dried under vacuum. The compound does not react readily with CO (1 atm., 25° C) in benzene solution. Yield, 0.2 g, 40%, m.p. 151-153° C (dec.). I.r. (Nujol), 1425m, 1355w, 1345w, 1295w, 1280w, 1245w, 1235w, 940s, 905w, 870s, 850s, 835w, 815w, 735m, 710m, 665m; I.r. (voltalef 3S) 2940m, 2900m, 2860m, 1510m, 1430s, 1350m.

(1.C) μ-(Dimethylsilanediyl)dimethylene-bis(trimethylsilylmethyl)-molybdiotris(trimethylphosphine)molybdenum(I,III) (Mo-Mo)

Bis(trimethylsilylmethyl)magnesium (4.0 cm^3 of a 0.9 M diethyl ether solution, 0.0036 mol) was added to $Mo_2(O_2CMe)_4$, (0.36 g, 0.00084 mol) suspended in diethyl ether (50 cm^3) and trimethylphosphine (1 cm^3). The red suspension was stirred (2 h) at 0° C and then at room temperature (4 h). The colour of the solution gradually changed from red to deep maroon to blue. It was evaporated and the red residue was dissolved in petroleum (50 cm^3), the solution filtered and concentrated to ca. 10 cm^3 to give red-brown needles on cooling (-20° C). Yield, 0.45 g, 50%, m.p. 143-145° C. I.r. (Nujol) 1420m, 1298m, 1280m, 1242s, 945s, 845s, 740bm, 720bm, 705bm, 670bm (cm^{-1}). The i.r. spectrum of (1.B) is virtually

identical with that of (1.C) except for the strong band at 1242 cm^{-1} in the latter.

The complex reacted with CO (1 atm, room temperature) in petroleum affording a solid (insoluble in petroleum, soluble in PhMe). The i.r. contained only terminal carbonyl absorptions and the ^1H n.m.r. showed only PMe_3 resonances and none due to Me_3SiCH_2. A red oil was produced with NO and the complex also reacted with CF_3CO_2H yielding a solution containing broad PMe_3 and Me_3SiCH_2 resonances in the ^1H n.m.r.. The i.r. (1770 cm^{-1}, $CF_3CO_2^-$) revealed bridging and unidentate acetates (1680, 1600 cm^{-1}).

(1.D) Bis-μ-acetatobis[trimethylphosphine(2,2-dimethylpropyl)-molybdenum(II)] (Mo-Mo)

Bis(2,2-dimethylpropyl)magnesium (3.8 cm^3 of a 1.1 M diethyl ether solution, 0.0042 mol) was added to $Mo_2(O_2CMe)_4$ (0.90 g, 0.0021 mol) suspended in diethyl ether (50 cm^3) and trimethylphosphine (1 cm^3). The mixture was stirred 1 h at 0° C and then at room temperature (3 h). The volatile material was removed in vacuum and the residue was extracted into petroleum (50 cm^3). The dark red-brown solution was filtered and the filtrate concentrated to ca. 10 cm^3. It was refiltered and cooled (-20° C). The red prisms were collected, washed (2 x 2 cm^3 cold petroleum) and dried in vacuum. Yield, 0.7 g, 55%; m.p. ca. 140° C (dec.). I.r. (Nujol) 1510m, 1425s, 1302w, 1283m, 1225m, 1208w, 948s, 844w, 838w, 740m, 725m, 668s (cm^{-1}). Note: $Mo_2(O_2CMe)_4$ has absorptions at 1510, 1495 and 1410 cm^{-1}.

The reaction of $Mo_2(O_2CMe)_4$ with ten molar equivalents of $Mg(Bu^tCH_2)_2$ in the presence of PMe_3 yields a dark green petroleum soluble oily material which could not be crystallised nor chromatographed ($A\ell_2O_3$, SiO_2 or cellulose) although it sublimed with decomposition (10^{-2} mmHg,

80-90^{o} C), it has not been obtained pure. The ^{1}H n.m.r. contains no resonances due to acetate.

Table 1.1

Analytical Data for Alkyl Compounds

Compound		Colour	M.P. θ_i/°C	Found				Required			
				C	H	P	M [a]	C	H	P	M
(1.A)	$Cr_2(CH_2SiMe_3)_4(PMe_3)_2$	Deep Red	80-100 d [b]	43.0	10.2	10.1	560	44.0	9.7	10.3	605
(1.B)	$Mo_2(CH_2SiMe_3)_2(O_2CMe)_2(PMe_3)_2$	Orange	151-3 d	34.3	7.3	9.8	-	34.0	7.2	9.8	-
(1.C)	$Mo_2(CH_2SiMe_3)_2((CH_2)_2SiMe_2)(PMe_3)_3$	Red	143-5	36.3	8.1	14.5	619	37.1	8.7	13.7	680
(1.D)	$Mo_2(CH_2CMe_3)_2(O_2CMe)_2(PMe_3)_2$	Red	130-50 d	40.2	7.9	8.8	589	39.8	7.6	10.3	604

[a] Cryoscopically in benzene.

[b] d = decomposed.

Table 1.2

^{1}H and $^{13}C\{H\}$ Nuclear Magnetic Resonance Spectra of Alkyl Compounds

Compound	δ values [a]	J_{H-P}, Hz	Assignment	$^{13}C\{H\}$ [b]	J_{C-P}, Hz
(1.A) $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$	1.25 s (1)		PMe_3	16.60 s	
	0.58 s (1)		μ-CH_2SiMe_3 [c]	5.25 s	
	0.25 s (1)		CH_2SiMe_3 [c]	6.86 s	
(1.B) $Mo_2(CH_2SiMe_3)_2(O_2CMe)_2(PMe_3)_2$	2.60 s (3)		O_2CMe	23.36 s	
	1.10 d (9)	$^{2}J_{H-P}$, 6	PMe_3	12.63 d	20.4
	0.25 s (9)		CH_2SiMe_3	3.99 s	
	[d]		O_2CMe	182.40 s	
			CH_2SiMe_3	9.05 d	29.2
(1.C) $Mo_2(CH_2SiMe_3)_2((CH_2)_2SiMe_2)(PMe_3)_3$	1.30 m (27)		PMe_3	23.67 d	17.5
				16.84 t	18.2
			CH_2SiMe_3	43.81 s	
	0.28 s (18)		CH_2SiMe_3	3.46 s	
			$(CH_2)_2SiMe_2$	73.62 s	
	0.84 s (8) [e]		$(CH_2)_2SiMe_2$	8.93 s	

Table 1.2 [continued]

Compound	δ values [a]	J_{H-P}, Hz	Assignment	$^{13}C\{H\}$ [b]	J_{C-P}, Hz
(1.D) $Mo_2(CH_2CMe_3)_2(O_2CMe)_2(PMe_3)_2$	2.81 s (6)		O_2CMe	-1.92 s	
	1.24 d (36)	$^2J_{H-P}$, 6	PMe_3	-15.72 d	18.0
	1.21 s (18)		CH_2CMe_3	13.86 s	
			O_2CMe	193.91 s	
	1.96 s (4)		CH_2CMe_3	21.75 dd	30.0, 5.0
			CH_2CMe_3	11.97 s	
(1.E) $Mo_2Me_4(PMe_3)_4$	1.30 m (36)		PMe_3	16.5 t	9.3
	-0.37 t (12)	$^3J_{H-P}$, 6	Me	2.69 t	6.0
(1.F) $Mo_2Me_4(PMe_2Ph)_4$	6.45 m (20)		PMe_2Ph		
	0.93 t (24)	$^2J_{H-P}$, 6	PMe_2Ph		
	-0.80 t (12)	$^3J_{H-P}$, 6	Me		
(1.G) $Mo_2(CH_2SiMe_3)_2((CH_2)_2SiMe_2)(P(OMe)_3)_3$	3.60 d	J_{H-P}, 9	$P(OMe)_3$	52.22 d	12.7
	3.46 t (27)	J_{H-P}, 9		14.98 m	
			CH_2SiMe_3	73.19 s	
	0.25 s (24)		CH_2SiMe_3	3.63 s	
			$(CH_2)_2SiMe_2$	79.87 s	
	0.89 s (8)		$(CH_2)_2SiMe_2$	8.35 s	

Table 1.2 [continued]

Compound	δ values [a]	J_{H-P}, Hz	Assignment	$^{13}C\{H\}$ [b]	J_{C-P}, Hz
(1.H) cis-$RuMe_2(PMe_3)_4$	1.20 d (18)	$^2J_{H-P}$, 4.8	cis-PMe_3	25.39 t	17.3
	1.21 t (18)	$^2J_{H-P}$, 4.8	trans-PMe_3	19.76 tt	23.7, 2.4
	-0.30 td (6)	$^3J_{H-P}$, 8 (cis P)	MeRu	-3.38 dq	63.8, 12.6
		$^3J_{H-P}$, 4 (trans p)			
(1.I) $Ru((CH_2)_2SiMe_2)(PMe_3)_4$	1.13 d (18)	$^2J_{H-P}$, 6	cis-PMe_3	25.54 t	19.4
	1.43 t (18)	$^2J_{H-P}$, 5	trans-PMe_3	22.10 tt	22.6, 3.6
	0.56 s (6)		$(CH_2)_2SiMe_2$	10.36 t	2.7
	-1.36 t (4)	$^3J_{H-P}$, 11	$(CH_2)_2SiMe_2$	-28.98 dq	46.0, 7.7
(1.J) $Ru((CH_2)_2CMe_2)(PMe_3)_4$	1.3 m				
(1.K) fac-$RhMe_3(PMe_3)_3$	1.10 d (27)	$^2J_{H-P}$, 5	PMe_3	18.71 td [g]	20.2, 1.9
	0.40 bd (9) [f]	J_{H-P}, 12	MeRh	7.64 bd	100.0
(1.L) $Rh(CH_2SiMe_3)((CH_2)_2SiMe_2)(PMe_3)_3$	1.13 t (27)	J_{H-P}, 12	PMe_3	20.12 m	
	0.60 s (3)		$(CH_2)_2SiMe_2$	10.78 s	
	0.42 s (3)			8.41 s	
	0.50 s (2)		$(CH_2)_2SiMe_2$		
	0.13 s (2)			-16.12 bd	72.7
	-0.80 bd (2) [h]	J, 8	CH_2SiMe_3		
	0.54 s (9)		CH_2SiMe_3	6.9 s	

Table 1.2 [continued]

Notes: Table 1.2

[a] Measured in benzene as solvent and internal reference (δ 7.27) and referenced to Me_4Si (δ 0.0) at 60 MHz and 35° C. Relative intensity ( ).

[b] Measured in benzene-d_6 as solvent and internal reference (δ 128.7) and referenced to Me_4Si (δ 0.0) at 25.2 MHz. Peaks to high frequency (low field) of Me_4Si are taken as positive.

[c] These assignments may be reversed.

[d] Not observed. Resonances due to CH_2SiMe_3 are probably masked by other peaks.

[e] See text.

[f] Broad doublet, possibly due to splitting by phosphorus nucleii trans to Me. Further splitting by Rh and cis P atoms not resolved.

[g] As for (1.H). Broad doublet from trans P coupling (J 100 Hz). Further splitting by Rh and cis P atoms not resolved.

[h] At 0° C a doublet of doublets is obtained (J_{H-Rh}, 9 Hz) and (J_{H-P}, 6 Hz).

Table 1.3 $^{31}P\{H\}$ N.M.R. Spectra of Alkyl Compounds

Compound	$^{31}P\{H\}$ [a]	J_{P-P} Hz	J_{P-Rh} Hz
(1.A) $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$	-17.35 [b]	-	
(1.B) $Mo_2(CH_2SiMe_3)_2(O_2CMe)_2(PMe_3)_2$	-11.51 s	-	
(1.C) $Mo_2(CH_2SiMe_3)_2((CH_2)_2SiMe_2)(PMe_3)_3$	- 0.83 d - 4.24 t	10.2 21.2	
(1.D) $Mo_2(CH_2CMe_3)_2(O_2CMe)_2(PMe_3)_2$	-16.38 s	-	
(1.E) $Mo_2Me_4(PMe_3)_4$	- 1.88 s	-	
(1.F) $Mo_2Me_4(PMe_2Ph)_4$	-	-	
(1.G) $Mo_2(CH_2SiMe_3)_2((CH_2)_2SiMe_2)(P(OMe_3)_3$	-17.4 d -35.2 t	35.1 34.0	
(1.H) cis-$RuMe_2(PMe_3)_4$	- 1.08 t -11.64 t	25.5 26.0	
(1.I) $Ru((CH_2)_2SiMe_2)(PMe_3)_4$	- 6.21 t -17.2 t	29.4 29.6	
(1.J) $Ru((CH_2)_2CMe_2)(PMe_3)_4$	- 5.50 t [c] -20.67 t	27.9 27.8	
(1.K) fac-$RhMe_3(PMe_3)_3$	-17.9 d	-	82.8
(1.L) $Rh(CH_2SiMe_3)((CH_2)_2SiMe_2)(PMe_3)_3$	-17.8 ddt -22.7 dd	18.9 18.9	91.1 86.3

[a] Measured in benzene-d_6 (10%)/benzene and referenced to external 85% H_3PO_4 (δ 0.0) at 40.5 M Hz. Peaks to high frequency (low field) of reference are taken as positive. [b] Benzene-d_6 (10%)/toluene at -80° C. [c] Benzene-d_6 (10%)/thf.

EXPERIMENTAL CHAPTER 2

(2.A) Tris(phenyl)-μ-acetatotris(trimethylphosphine)dimolybdenum(II) (Mo-Mo)

Diphenylmagnesium (3.8 cm^3 of a 0.7 M diethyl ether solution, 2.7 mmol) was added to $Mo_2(O_2CMe)_4$ (0.57 g, 1.3 mmol) suspended in diethyl ether (50 cm^3) and trimethylphosphine (1 cm^3) at 0^o C.

The solution rapidly became dark blue-green; after stirring (1 h) at 0^o C, volatile material was removed in vacuum and the blue residue extracted into petroleum (40 cm^3). The solution was filtered, concentrated to ca. 20 cm^3 and cooled (-20^o C) to give dark blue prisms which were washed with cold petroleum (1 cm^3) and dried in vacuum. Yield 0.4 g, 46%; m.p. 151-3^o C. I.r. (Nujol) 3030m, 1557m, 1545w, 1512m, 1465s, 1420s, 1365w, 1345w, 1300m, 1280s, 1275m, 1235w, 1040w, 1010w, 942sbr, 845m, 735m, 720s, 704s, 672m cm^{-1}. A similar reaction in the absence of phosphine or using other phosphines (PMe_2Ph, $PPhMe_2$) lead only to decomposition.

The compound is stable in air for ca. 15 mins but decomposes immediately in solution when exposed to the atmosphere. It does not react with H_2, C_2H_4 (1 atm, room temperature) but does so with NO, CO, MeC_2H, C_2H_2 and PhC_2H in benzene to give red-brown materials although pure compounds could not be isolated. The compound did not sublime at 150^o C/10^{-2} mmHg and the remaining black solid did not redissolve in C_6H_6.

(2.B) Tris(4-fluorophenyl)-μ-acetato-tris(trimethylphosphine)dimolybdenum-(II) (Mo-Mo)

Di(4-fluorophenyl)magnesium (4.5 cm^3 of a 0.8 M Et_2O solution, 3.6 mmol) was added to $Mo_2(O_2CMe)_4$ (0.77 g, 1.8 mmol) suspended in diethyl

ether (50 cm^3) and trimethylphosphine (1 cm^3) at 0^o C. The solution was stirred (1 h) at 0^o C, evaporated to dryness under vacuum and the residue extracted into petroleum (40 cm^3), filtered and the solution reduced to ca. 30 cm^3. Cooling (-20^o C) yielded blue-green crystals which were washed with petroleum (2 x 2.5 cm^3) at -78^o C and dried under vacuum. A further batch of crystals was obtained from the original residue after extraction into petroleum (20 cm^3), filtration, evaporation (to ca. 10 cm^3) and cooling (-20^o C). Yield 0.4 g, 32%; m.p. 145-9^o C (dec.). I.r. (Nujol), 3050w, 1595w, 1560s, 1520w, 1491s, 1455s, 1430s, 1365w, 1345w, 1300w, 1282m, 1211s, 1155s, 1017w, 950s, 850w, 806m, 750m, 741w, 730w, 725w, 682w, 678m cm^{-1}.

Decomposition occurs in the absence of phosphine. The compound is less air sensitive than (2.A) and lasts for ca. 1 h in the solid state but again decomposes immediately in solution when exposed to the atmosphere.

Deuteration Experiments

To the crystalline phenyl and 4-fluorophenyl compounds above (ca. 0.1 g) was added ca. 2 cm^3 of 6 M D_2SO_4 in D_2O. After shaking with diethyl ether (2 x 5 cm) which was reduced to ca. 1 cm^3, mass spectroscopic analysis showed that only the monodeuterated arene was formed: m/e 79 (C_6H_5D); m/e 97 (C_6H_4DF) plus m/e 74 ($C_4H_{10}O$) and m/e 59 ($C_2H_3O_2^+$, acetate).

(2.C) Tetrakis(2-methoxyphenyl)bis(trimethylphosphine)dimolybdenum(II) (Mo-Mo) and

(2.D) Tetrakis(2-methoxyphenyl)dimolybdenum(II) (Mo-Mo)

Di(2-methoxyphenyl)magnesium (3.8 cm^3 of a 0.76 M diethyl ether

solution, 2.9 mmol) was added to $Mo_2(O_2CMe)_4$ (0.62 g, 1.4 mmol) suspended in diethyl ether (55 cm^3) and trimethylphosphine (1 cm^3) at -78° C. The solution was allowed to warm to 10° C (1 h) and stirred at this temperature (1 h). After evaporation to dryness the residue was extracted into petroleum (80 cm^3), filtered, snd the solution evaporated to ca. 30 cm^3. Cooling (-20° C) yielded deep blue-green needles which were washed with petroleum (2 x 2 cm^3) and dried under vacuum. Yield, 0.3 g, 28%; m.p. 75-80° C (dec.). I.r. (Nujol), 3030w, 1595m, 1550w, 1485s, 1450m, 1410m, 1295s, 1275m, 1243s, 1200m, 1155m, 1140m, 1036m, 1015m, 1000m, 945sbr, 845w, 778m, 750s, 708m, 689w cm^{-1}.

A solution of (2.C) (0.3 g, 0.39 mmol) was stirred in benzene at room temperature (24 h) and the pink precipitate of the complex (2.D) allowed to settle. The collected product was washed with thf (2 x 10 cm^3) and petroleum (10 cm^3) and dried under vacuum. Yield, 0.22 g, 90%; m.p. 220-40° C (dec.). I.r. (Nujol), 3030w, 1600w, 1585w, 1547w, 1495w, 1445s, 1439m, 1419m, 1365w, 1250s, 1245m, 1206m, 1195w, 1145m, 1090mbr, 1145m, 1110m, 995m, 800s, 756m, 746m, 718m cm^{-1}.

(2.E) Hexakis(2-methoxyphenyl)dirhenium(III) (Re-Re)

Di(2-methoxyphenyl)magnesium (3.5 cm^3 of a 0.76 M diethyl ether solution, 2.7 mmol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$ (0.60 g, 0.88 mmol) in diethyl ether (60 cm^3) at -10° C. The solution was then stirred (10 h) at room temperature, evaporated to dryness under vacuum and the residue extracted with dichloromethane (30 cm^3). The solution was filtered, evaporated to ca. 7 cm^3, and cooled (-20° C) to give dark green prisms which were recrystallised twice from CH_2Cl_2 (as above) washed with petroleum (5 cm^3) and dried under vacuum. Yield, 0.3 g, 34%; m.p. 180-200° C (dec). I.r. (KBr disc), 3065w, 3045m, 2940m, 2920m, 2880w, 2820m, 1568s, 1510m, 1450s, 1440s, 1419s, 1285w, 1562m,

1240s, 1217s, 1211s, 1165m, 1158s, 1111s, 1055w, 1045m, 1021m, 1007s, 923w, 840w, 790m, 784m, 775m, 752s, 747s, 740s, 718s, 592w, 570w, 530w, 470w, 450w, 442w cm^{-1}.

(2.F) cis-Diphenyltetrakis(trimethylphosphine)ruthenium(II)

Diphenylmagnesium (6.2 cm^3 of a 0.53 M diethyl ether solution, 3.3 mmol) was added to a suspension of $Ru_2(O_2CMe)_4Cl$ (0.64 g, 1.35 mmol) in tetrahydrofuran (50 cm^3) and trimethylphosphine (1 cm^3). The solution was stirred for 2 h (room temperature) and evaporated to dryness. The yellow residue was extracted into warm (50° C) petroleum and filtered while still warm. After evaporation to ca. 20 cm^3 and cooling (-20° C) the very pale yellow microcrystals were collected and washed with cold petroleum (2 x 2 cm^3) and dried under vacuum. They were recrystallised as off-white prisms from ca. 2 cm^3 of hot (ca. 50° C) benzene at room temperature. Yield, 0.4 g, 27%; m.p. 130-40° C (dec.). I.r. (petroleum solution; matched KBr cells under N_2); δ_{NN} = 2128 cm^{-1} s; (Nujol) 3090w, 2100s (see Text), 1550mbr, 1435sbr, 1295s, 1275s, 1179w, 1050m, 1005m, 930sbr, 850s, 730s, 700s, 655s, 630m cm^{-1}.

(2.G) (2-Methyleneoxaphenyldiyl)tetrakis(trimethylphosphine)ruthenium(II)

Di(2-methoxyphenyl)magnesium (8.5 cm^3 of a 0.33 M diethyl ether solution, 2.8 mmol) was added to $Ru_2(O_2CMe)_4Cl$ (0.4 g, 0.85 mmol) in tetrahydrofuran (40 cm^3) and PMe_3 (1 cm^3). The solution was stirred for 12 h (room temperature). Volatile material was removed in vacuum and the residue extracted into warm (50° C) petroleum (50 cm^3) and filtered. The yellow solution was evaporated to dryness and the residue dissolved in toluene (10 cm^3) and filtered.

The solution was transferred to a 15 x 2 cm " fluorosil" column which was eluted first with toluene (ca. 100 cm^3) and then with thf

(ca. 100 cm^3). The thf fraction was evaporated to dryness and the residue recrystallised from ca. 3 cm^3 of toluene (-20° C) to give white needles which were washed and dried as above. Yield 0.25 g, 29%. The compound turns yellow at ca. 175° C and becomes progressively more orange until ca. 240° C when it decomposes. I.r. (Nujol), 3025m, 1550w, 1442s, 1420s, 1365m, 1298s, 1288s, 1270s, 1245w, 1165s, 1093w, 1009m, 965m, 985sbr, 965ssh, 850s, 840m, 830w, 800m, 746m, 718s, 704s, 663s, 634w, 542w, 508w, 363s, 338w, 317w, 259w cm^{-1}.

(2.H) Phenyltris(trimethylphosphine)rhodium(I)

Trimethylphosphine (1 cm^3) was added to a suspension of $Rh_2(O_2CMe)_4$ (0.44 g, 0.99 mmol) in diethyl ether (40 cm^3) at 0° C. Diphenylmagnesium (2.9 cm^3 of a 0.7 M diethyl ether solution, 2 mmol) was added to the yellow-brown suspension which was stirred (4 h) at room temperature. The volatile material was removed in vacuum, the residue extracted into petroleum (40 cm^3) and the filtered solution evaporated to ca. 10 cm^3 and cooled (-20° C) yielding orange-yellow crystals. These were washed with cold petroleum (1 cm^3) and dried under vacuum. Yield, 0.3 g, 37%; m.p. 85-90° C (dec.). I.r. (Nujol), 3040w, 1570m, 1470s, 1420m, 1365m, 1300m, 1280m, 1175m, 1060w, 1018m, 940s, 850m, 818w, 732m, 708m, 665w cm^{-1}.

The compound reacts with hydrogen to give an initial dark orange solution which becomes pale yellow after ca. 5 min. (1 atm., room temperature). Benzene is liberated (^1H n.m.r.) and a broad resonance at ca. τ 19.3 in the ^1H n.m.r. indicates Rh-H bond formation although a pure compound was not isolated.

(2.I) 2-Methoxyphenyltris(trimethylphosphine)rhodium(I)

Trimethylphosphine (0.7 cm^3) was added to a suspension of

$Rh_2(O_2CMe)_4$ (0.43 g, 0.97 mmol) in diethyl ether (40 cm^3). Di(2-methoxyphenyl)magnesium (9.7 cm^3 of a 0.2 M diethyl ether solution, 1.9 mmol) was added and the suspension stirred (5 h) at room temperature.

The volatile material was removed in vacuum, the residue extracted with petroleum (50 cm^3) and the filtered solution was evaporated to ca. 3 cm^3 and cooled (-20° C) yielding a yellow solid. This was recrystallised from toluene (5 cm^3) at -20° C to give yellow crystals which were washed with petroleum (2 x 2 cm^2) and dried under vacuum. Yield, 0.4 g, 46%; m.p. 99-101° C. I.r. (Nujol), 3060w, 1571m, 1470sbr, 1450s, 1376s, 1376m, 1312m, 1288s, 1261w, 1182m, 1114w, 1029m, 980m, 953s, 872w, 863m, 850m, 817m, 770m, 760m, 737m, 730m, 677m cm^{-1}.

Table 2.1

Analytical Data for Aryl Compounds

Compound	Colour	Found %				Required %			
		C	H	P	M [a]	C	H	P	M [a]
(2.A) $Mo_2(O_2CMe)(C_6H_5)_3(PMe_3)_3$	Dark Blue	49.4	6.5	13.0 [b]	707	49.0	6.3	13.1	710
(2.B) $Mo_2(O_2CMe)(4F\text{-}C_6H_4)_3(PMe_3)_3$	Dark Blue	45.3	5.5	11.9 [c]	680	45.5	5.5	12.2	764
(2.C) $Mo_2(2MeO\text{-}C_6H_4)_4(PMe_3)_2$	Blue Green	53.5	6.5	7.0	384 [d]	52.8	6.0	8.0	772
(2.D) $Mo_2(2MeO\text{-}C_6H_4)_4$	Pink	53.8	4.5	< 0.2	594 [e]	54.2	4.5	0.0	620
(2.E) $Re_2(2MeO\text{-}C_6H_4)_6$	Dark Green	49.9	4.4	-	960 [f]	49.7	4.1	-	1014
(2.F) $Ru(C_6H_5)_2(PMe_3)_4$	Off-White	51.4	8.1	22.2	510	51.5	8.2	22.2	559
(2.G) $Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4$	White	44.6	8.3	24.3	508	44.6	8.2	24.3	511
(2.H) $Rh(C_6H_5)(PMe_3)_3$	Orange	44.4	8.0	23.4	408	44.1	7.8	22.8	408
(2.I) $Rh(2MeO\text{-}C_6H_4)(PMe_3)_3$	Yellow	44.7	7.7	19.4	455	43.8	7.8	21.2	438

[a] Cryostopically in benzene;

[b] Mo, found 25.6 (required 27.0);

[c] F, found 7.3 (required 7.5);

[d] See text;

[e] Cryoscopically in Me_2SO;

[f] Osmometrically in $CH_2C\ell_2$.

Table 2.2

^{1}H and ^{13}C Nuclear Magnetic Resonance Data of Aryl Compounds

Compound	^{1}H δ values [a]	Assignment	$^{13}C\{^{1}H\}$ [b]
(2.A) $Mo_2(O_2CMe)(C_6H_5)_3(PMe_3)_3$	8.50-7.20 b (15) 2.55,2.40[c] s (3) 1.15-0.55 m (27)	C_6H_5 O_2CMe PMe_3	182.73 bs (O_2CMe), 142.88 to 141.33 m and 127.29 to 124.68 m (C_6H_5), 24.77, 24.47 [c] s (O_2CMe), 18.72 to 13.28 m (PMe_3)
(2.B) $Mo_2(O_2CMe)(4\text{-}FC_6H_4)_3(PMe_3)_3$	7.45-6.72 b (15) 2.34,2.43[d] s (3) 1.10-0.50 m (27)	$4\text{-}FC_6H_4$ O_2CMe PMe_3	183.29 [e] s (O_2CMe), 143.47 to 142.18 m, 114.18 to 112.62 m, ($4\text{-}FC_6H_4$), 24.71, 24.35 s (O_2CMe), 18.49-13.04 m (PMe_3)
(2.C) $Mo_2(2\text{-}MeOC_6H_4)_4(PMe_3)_2$	8.15-7.35 b (16) 4.70 s (12) 2.30-1.65 m (18)	($2\text{-}MeOC_6H_4$) ($2\text{-}MeOC_6H_4$) PMe_3	-
(2.D) $Mo_2(2\text{-}MeOC_6H_4)_4$	7.40-6.60 b (4) 3.70 s (3)	($2\text{-}MeOC_6H_4$) ($2\text{-}MeOC_6H_4$)	-

Table 2.2 [continued]

Compound	^1H δ values [a]	Assignment	$^{13}C\{^1H\}$ [b]
(2.E) $Re_2(2\text{-}MeOC_6H_4)_6$	8.25-6.60 b (24) 3.20 s (18)	2-$MeOC_6H_4$ 2-$\underline{Me}OC_6H_4$	[f] 141.5, 130.56, 128.46, 127.21, 120.52, 119.83, 111.44, 108.41 s (2-$MeO\underline{C}_6H_4$), 55.54, 54.09 [c] s (2-$\underline{Me}OC_6H_4$)
(2.F) $Ru(C_6H_5)_2(PMe_3)_4$	8.07-7.12 b (10) 1.24 s (36)	C_6H_5 PMe_3	-
(2.G) $Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4$	8.00-6.95 b (4) 5.35 [g] t.d.d. (2) 1.45-1.05 m (36)	(2-$CH_2OC_6H_4$) 2-$CH_2OC_6H_4$ PMe_3	-
(2.H) $Rh(C_6H_5)(PMe_3)_3$	8.10-7.15 b (5) 1.29 s (27)	C_6H_5 PMe_3	-
(2.I) $Rh(2\text{-}MeOC_6H_4)(PMe_3)_3$	7.60-6.70 b (4) 3.83 s (3) 1.20 bs (27)	2-$MeO_6C_6H_4$ 2-$\underline{Me}OC_6H_4$ PMe_3	-

[a] In benzene-d_6 as solvent with Me_4Si as internal reference, referenced to Me_4Si (δ 0.0) at 60 MHz and 35° C. Relative intensity ( ). b = broad, m = multiplet; [b] In benzene-d_6 as solvent and internal reference (δ 128.7), referenced to Me_4Si (δ 0.0) at 25.2 MHz at 28° C. Peaks to high frequency of Me_4Si are positive; [c] Relative intensity ca. 1 : 2; [d] Relative intensity ca. 1 : 1; [e] See ref. 15 for $^{13}C\{^1H\}$ data on bridging acetates; [f] In $CD_2C\ell_2$ as solvent and internal reference (δ 76.9), referenced to Me_4Si (δ 0.0) at 25.2 MHz at 28°C; [g] $J_{^{31}P-^1H}$ = 15 Hz (cis), $J_{^{31}P-^1H}$ = 5, 2 Hz (trans).

Table 2.3

$^{31}P\{^{1}H\}$ Nuclear Magnetic Resonance Data

Compound	δ Values [a]
(2.A) $Mo_2(O_2CMe)(C_6H_5)_3(PMe_3)_3$	AB$_2$ [b] δ_A -9.80, δ_B -8.73, J_{AB} = 17.5 Hz
	AMX δ_A -12.51, δ_M -16.79, δ_X -19.19 J_{AX} = 16.9, J_{AM} = 13.8, J_{MX} = 7.5 Hz
(2.B) $Mo_2(O_2CMe)(4\text{-}FC_6H_4)_3(PMe_3)_3$	AB$_2$ δ_A -10.77, δ_B -9.36, J_{AB} = 18.8 Hz
	AMX δ_A -13.21, δ_M -16.69, δ_X -19.44 J_{AX} = 17.6, J_{AM} = 12.8, J_{MX} = 7.5 Hz
(2.C) $Mo_2(2\text{-}MeOC_6H_4)_4(PMe_3)_2$	5.13 s 6.50 s [c]
(2.F) $Ru(C_6H_5)_2(PMe_3)_4$	-9.13 s
	A_2X_2 [d] δ_A -7.02, δ_X -19.04, J_{AX} = 23.4 Hz
	AX$_2$ δ_A -13.79, δ_X -8.86, J_{AX} = 22.8 Hz
(2.G) $Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4$	[e] δ_A -5.95 d.d δ_B -14.32 t.d. δ_C -20.07 t.d.
(2.H) $Rh(C_6H_5)(PMe_3)_3$	-16.33 d $J_{103Rh-31P}$ = 142.1 Hz -21.09 to -12.95 m [f]
(2.I) $Rh(2\text{-}MeOC_6H_4)(PMe_3)_3$	-15.65 d $J_{103Rh-31P}$ = 146.2 Hz -12.16 to -19.41 m [f]

[a] In benzene/10% benzene-d_6 and referenced to external 85% H_3PO_4 (δ 0.0) at 40.5 MHz. Peaks to high frequency of reference are positive.
[b] 0° C in toluene/10% C_6D_6. [c] At -40° C in Et_2O/10% C_6D_6. [d] At -40° C in thf/10% C_6D_6. [e] Labelling as in (VII); $J_{P_A-P_B}$ = 25.2 Hz, $J_{P_A-P_C}$ = 27.9 Hz, $J_{P_B-P_C}$ = 14.8 Hz, P_B and P_C may be reversed. [f] At -40°C in toluene/10% C_6D_6, complex patterns of at least 12 lines (2.H) and 18 lines (2.I) are observed.

EXPERIMENTAL CHAPTER 3

(3.A) Bis(acetato methyl)bis-μ-acetatodirhenium(III)

A deoxygenated mixture of glacial acetic acid (35 cm^3) and acetic anhydride (5 cm^3) was added to solid $Li_2Re_2Me_8.2Et_2O$, at -196° C, obtained from rhenium pentachloride (6.04 g, 0.0167 mol) and methyl lithium (125 cm^3 of a 1.0 M diethyl ether solution, 0.125 mol) as previously described.[13] The mixture was allowed to warm slowly to room temperature (over 10 h) and distilled water (50 cm^3) was added. The red brown slurry was stirred (2 h) and filtered on a sintered glass frit. The residue was extracted into dichloromethane (10 x 20 cm^3); the filtrates were collected and the solvent removed under vacuum. The pink residue was recrystallised from boiling glacial acetic to give red prisms. Yield 2.0 g, 38% based on $ReCl_5$. [Note: the yield of $Li_2Re_2Me_8.2Et_2O$ from $ReCl_5$ is only ca. 50%.[13]] The compound does not have a sharp melting point but decomposes over the range 200-250° C. I.r. (Nujol) cm^{-1}: 1555s, 1450sbr, 1395s, 1375s, 1365s, 1352s, 1342s, 1155w, 1045m, 1010m, 934m, 692s, 676s, 638w, 617w, 545m, 540m, 480w, 372m, 339m, 332w, 305w, 289m. ^1H n.m.r. ($CDCl_3$) δ 3.23s(6), 2.35s(6), 1.80s(6).

The compound is moderately soluble in CH_2Cl_2, $CHCl_3$ and C_6H_6 but virtually insoluble in acetone, CS_2 and thf. It decomposes in pyridine and tetramethylethylenediamine giving green brown materials, and also when warmed in ethanol, water, dimethylsulphoxide, dimethylformamide, and "880" ammonia giving red brown solutions. The action of MeSH and H_2S on CH_2Cl_2 solutions also results in decomposition. It does not react with CO, H_2, ethylene or SO_2 under ambient conditions (1 atm., room temperature) and appears to be indefinitely air stable.

(3.B) Bis(chloromethyl)bis-μ-acetatodirhenium(III) and its dimethylsulphoxide adduct (3.C)

Chlorine gas was passed slowly through a solution of (3.A) (0.1 g, 0.00016 mol) in dichloromethane (15 cm^3) for 5 min. The purple powder was collected, washed with diethyl ether (2 x 5 cm^3) and dried under vacuum. I.r. (Nujol) cm^{-1}: 1470s, 1450s, 1385s, 1370m, 1350m, 1210w, 1170w, 1035m, 1025m, 735m, 680s, 630w, 530m, 380m, 340w, 295m, 280m.

Red crystals of the dimethylsulphoxide adduct $Re_2Me_2Cl_2(O_2CMe)_2.Me_2SO$ (3.C), were obtained from (3.B), (0.1 g, 0.00016 mol) warmed in dimethylsulphoxide (2 cm^3) after several days at room temperature. They were collected, washed with acetone (2 x 0.5 cm^3) and dried under vacuum. I.r. (Nujol) cm^{-1}: 1465sbr, 1440sbr, 1400sbr, 1375s, 1365s, 1350m, 1340m, 1310w, 1290w, 1210w, 1192w, 1020m, 983s, 945s, 931s, 717w, 675s, 627w, 545m, 530w, 405m, 395w, 375w, 368m, 350w, 335m, 325w, 291m, 289m, 280w, 265w. Yields of (3.B) and (3.C) were almost quantitative.

(3.C) was also prepared as follows. A deoxygenated mixture of glacial acetic acid (4 cm^3) and acetic anhydride (0.5 cm^3) was added to a solution of $Li_2Re_2Me_8$ in diethyl ether, prepared from rhenium pentachloride (1.28 g) and methyl lithium (6 equivalents) (as above) at -50° C. The stirred solution was allowed to warm to room temperature and evaporated to dryness under vacuum. The residue was washed with dichloromethane (150 cm^3) and collected. The material is insoluble in most solvents and could not be purified by crystallisation or other means. However, with dimethylsulphoxide, crystals of (3.C) were obtained after several days at room temperature.

(3.D) Methylmethoxy-μ-acetatorhenium(III)

(3.A) (0.1 g, 0.0016 mol) was warmed (50° C) in methanol (25 cm^3)

for 5 min. The mauve powder was filtered, washed with diethyl ether and dried under vacuum. I.r. (Nujol) cm^{-1}: 1490m, 1445s, 1405s, 1360m, 1350m, 1040w, 1020s, 750w, 720w, 675s, 630w. Yield: ca. 100%.

(3.E) Tetrakis(trimethylsilylmethyl)bis-μ-acetatodirhenium(III)

Bis(trimethylsilylmethyl)magnesium (1.4 cm^3 of a 1.0 M diethyl ether solution, 0.0014 mol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$, (0.32 g, 0.00047 mol) suspended in diethyl ether (30 cm^3). After stirring for 10 h the solvent was evaporated and the red-brown residue extracted into petroleum (50 cm^3). The solution was filtered and evaporated to ca. 5 cm^3 and cooled (-20° C). The red needles were collected and dried under vacuum. Yield 0.2 g, 51%. I.r. (Nujol) cm^{-1}: 1357w, 1335w, 1260s, 1245s, 980m, 940m, 910w, 850s, 825s, 745m, 725m, 705m, 680m, 673s.

(3.F) Tetrakis(2,2-dimethylpropyl)bis-μ-acetatodirhenium(III)

Bis(2,2-dimethylpropyl)magnesium (5.7 cm^3 of a 0.61 M diethyl ether solution, 0.00348 mol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$ (0.79 g, 0.00116 mol) in diethyl ether (50 cm^3) at 0° C. The mixture was stirred (10 h) at room temperature then evaporated to dryness and the residue extracted into petroleum (50 cm^3) and filtered. The filtrate was concentrated (20 cm^3), refiltered and cooled (-20° C), yielding deep red crystals. They were washed with cold petroleum (2 x 1 cm^3) and dried under vacuum. Yield 0.5 g, 45%. I.r. (Nujol) cm^{-1}: 1465sbr, 1435sbr, 1420s, 1375s, 1360s, 1350s, 1345s, 1265w, 1227s, 1105w, 1030w, 1005w, 920w, 742m, 735m, 720w, 705w, 664s, 620m, 585m, 560s.

(3.G) Tetrakis(2-methyl-2-phenylpropyl)bis-μ-acetatodirhenium(III)

Bis(2-methyl-2-phenylpropyl)magnesium (3.4 cm^3 of a 1.0 M diethyl

ether solution, 0.0034 mol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$ (0.76 g, 0.0011 mol) in diethyl ether (75 cm^3) at -78° C. The suspension was stirred and allowed to warm slowly to room temperature (10 h) and then stirred for an extra 24 h. The mixture was evaporated to dryness and washed with petroleum (50 cm^3). The remaining pink residue was dried under vacuum and extracted into dichloromethane (60 cm^3). The solution was filtered and evaporated to ca. 15 cm^3 under vacuum. A pink powder was deposited which was redissolved by warming the solution briefly to ca. 50°C. Cooling (-20° C) yielded red prisms. They were washed with petroleum (5 cm^3) and dried under vacuum. Yield 0.4 g, 34%. I.r. (Nujol) cm^{-1}: 3080w, 3050w, 3020w, 1595w, 1493m, 1465sbr, 1455sbr, 1435s, 1420m, 1405w, 1375s, 1360m, 1350m, 1275w, 1190m, 1025w, 765s, 700s, 667s, 625m, 585m.

(3.H) Tetrakis(benzyl)bis-μ-acetatodirhenium(III)

Dibenzyl magnesium (1.0 cm^3 of a 0.94 M diethyl ether solution 0.00094 mol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$ (0.24 g, 0.00035 mol) in diethyl ether (40 cm^3) at -78° C. The suspension was warmed to 0° C and stirred at room temperature for 20 min. The solution was filtered and evaporated to dryness. The residue was extracted into diethyl ether (30 cm^3) and filtered. The filtrate was evaporated to ca. 15 cm^3 and cooled (-20° C) yielding dark purple crystals. Yield 0.15 g, 50%. I.r. (Nujol) cm^{-1}: 3070w, 3050w, 3010w, 1590m, 1495m, 1465sbr, 1455sbr, 1445s, 1375s, 1365m, 1350m, 1260w, 1207m, 1197w, 1175w, 1025w, 800w, 755s, 745m, 720w, 700s, 667s, 625w.

Table 3.1

Analytical Data for Re(III) Alkyls

Compound	Colour	M.P. [b] θ_i/°C	Found				Required			
			C	H	Re	M [a]	C	H	Re	M
(3.A) $Re_2Me_2(O_2CMe)_4$	Red	200-50 d	19.1	2.9	-	720	18.8	2.8	-	638
(3.B) $\{ReMe(O_2CMe)Cl\}_n$	Purple	260-70 d	12,5	2,0	12,7[c]	-	12.2	2.0	12.0[c]	-
(3.C) $Re_2Me_2(O_2CMe)_2Cl_2.Me_2SO$	Red	260-70 d	15.0	2.9	10.0[c]	-	14.3	2.7	10.6	-
(3.D) $\{ReMe(OMe)(O_2CMe)\}_n$	Mauve	100-20 d	17.0	3.3	63.5	-	16.5	3.2	63.9	-
(3.E) $Re_2(CH_2SiMe_3)_4(O_2CMe)_2$	Red	135-7	29.3	6.3	-	877	28.6	6.0	-	838
(3.F) $Re_2(CH_2CMe_3)_4(O_2CMe)_2$	Red	158-60	37.3	6.6	47.6	680	37.2	6.5	48.1	774
(3.G) $Re_2(CH_2CMe_2Ph)_4(O_2CMe)_2$	Red	178-80	50.5	5.6	34.6	950	49.7	5.5	35.0	1062
(3.H) $Re_2(CH_2Ph)_4(O_2CMe)_2$	Purple	156-8	44.2	4.2	-	-	45.0	4.0	-	-

[a] Cryoscopically in benzene.

[b] Many of the compounds decompose gradually over a wide range of temperature.

[c] Chlorine.

Table 3.2 ^{1}H and $^{13}C\{^{1}H\}$ N.M.R. Data for $Re_2R_4(O_2CMe)_2$ Compounds

Compound	^{1}H n.m.r. (δ)[a]	Assignment	$^{13}C\{^{1}H\}$ n.m.r.[b]
(3.E) $Re_2(CH_2SiMe_3)_4(O_2CMe)_2$	2.50s(6)	μ-$O_2C\underline{Me}$	22.36s
	1.84s(8)	$Re\underline{CH_2}SiMe_3$	33.70s
	0.30s(36)	$ReCH_2Si\underline{Me_3}$	3.57s
		μ-$O_2\underline{C}Me$	187.19s
(3.F) $Re_2(CH_2CMe_3)_4(O_2CMe)_2$	2.52s(6)	μ-$O_2C\underline{Me}$	21.76s
	2.71s(8)	$Re\underline{CH_2}CMe_3$	60.49s
	1.32s(36)	$ReCH_2C\underline{Me_3}$	35.15s
		$ReCH_2\underline{C}Me_3$	35.95s
		μ-$O_2\underline{C}Me$	186.76s
(3.G) $Re_2(CH_2CMe_2Ph)_4(O_2CMe)_2$	2.27s(6)	μ-$O_2C\underline{Me}$	21.58s[c]
	2.85s(8)	$Re\underline{CH_2}CMe_2Ph$	59.15s
	1.40s(24)	$ReCH_2C\underline{Me_2}Ph$	32.92s
	7.1-7.7 b(20)	$ReCH_2CMe_2\underline{Ph}$	125.05s
			125.89s
			127.90s
			153.91s
		$ReCH_2\underline{C}Me_2Ph$	41.36s
		μ-$O_2\underline{C}Me$	185.81s
(3.H) $Re_2(CH_2Ph)_4(O_2CMe)_2$	2.71s(6)[d]	μ-$O_2C\underline{Me}$	21.49s[c]
	3.33s(8)	$Re\text{-}\underline{CH_2}Ph$	40.36s
	6.5-7.3 b(20)	$Re\text{-}CH_2\underline{Ph}$	123.90
			128.08
			129.76
			142.78
		μ-$O_2\underline{C}Me$	187.39

[a] Benzene solvent and internal reference (δ 7.27) and referenced to Me_4Si (δ 0.0) at 60 MHz and 35° C. Relative intensity ( ).

[b] Benzene-d_6 solvent and internal reference (δ 128.7) and referenced to Me_4Si (δ 0.0) at 25.2 MHz. Peaks to high frequency (low field) of Me_4Si are positive.

[c] Chloroform-d_1 solvent and internal reference (δ 76.9) and referenced to Me_4Si (δ 0.0) at 25.2 MHz.

[d] Chloroform-d_1 solvent with Me_4Si (δ 0.0) as internal reference.

Experimental Chapter 4

(4.A) Hexakis(trimethylphosphine)tris-μ-methylenediruthenium(III) (Ru-Ru)

Dimethylmagnesium (70.0 cm^3 of a 1.1 M diethyl ether solution, 0.077 mol) was slowly added (10 min) to a suspension of $[Ru_3O(O_2CMe)_6.(H_2O)_3](O_2CMe)$ (5.0 g, 0.00636 mol) in tetrahydrofuran (250 cm^3) and trimethylphosphine (5.0 cm^3) at -20° C. The solution was allowed to warm slowly (1 h) and stirred at room temperature (48 h). Methane (by infrared) is evolved. The solution was evaporated under vacuum, the residue extracted with petroleum (200 cm^3) and the solution filtered. On reduction of the filtrate to ca. 50 cm^3 and cooling (-20° C) dark orange-red prisms were obtained. These were filtered, washed with petroleum (2 x 3 cm^3) at -78° C, and dried under vacuum. A further batch of (4.A) could be obtained by evaporation of the filtrate or by re-extraction of the residue with petroleum (2 x 200 cm^3), etc.. Overall yield, 1.8 g, 27% based on Ru content of $[Ru_3O(O_2CMe)_6.(H_2O)_3](O_2CMe)$; m.p., 186-8° C.

I.r. (Nujol) : 1455s, 1435m, 1420w, 1411m, 1361w, 1285s, 1270s, 926sbr, 835m, 715w, 696s, 650s, cm^{-1}. In air the compound decomposes in ca. 12 h (solid state) and within seconds (in solution).

It is soluble in hydrocarbon solvents, THF and diethyl ether without decomposition, insoluble in acetone, nitromethane, acetonitrile and water; it decomposes rapidly in $CHC\ell_3$ or $CH_2C\ell_2$. The compound does not react with H_2, CO, or C_2H_4 (1 atm., room temperature) and was recovered unchanged from reactions with ^nBuLi, MeLi and Na/Hg in THF. With NO an orange-brown solid is obtained which is insoluble in petroleum, toluene, but soluble in $CH_2C\ell_2$; with SO_2 an orange powder is formed.

Note: Lower yields of (4.A) resulted if less PMe_3 or Me_2Mg than indicated above is used in its preparation. Lower yields also resulted

when less solvent was used or when the reaction was stopped before ca. 48 h. (4.A) could not be obtained in higher yields from the reaction of $Ru_2^{II,III}(O_2CMe)_4Cl$ with Me_2Mg and PMe_3 by variations of the reaction conditions or stoichiometries. Low yields (ca. 5%) of cis-$-RuMe_2(PMe_3)_4$ are also obtained from the reaction with $[Ru_3O(O_2CMe)_6(H_2O)](O_2CMe)$. Other Ru_3 oxo centered species such as $[Ru_3O(OBu^t)_6(Mepy)_3]ClO_4$ or $[Ru_3O(O_2CMe)_6(P(OPh)_3)_3]$ were not good starting materials for the preparation of (4.A); only very low yields resulted using similar conditions to those described above.

Refluxing cis-$Ru(PMe_3)_4Me_2$ in toluene (48 h) or heating in benzene in a sealed tube for 48 h at 150° C, or the use of u.v. irradiation failed to produce (4.A) despite the formation of homogeneous red solutions in both cases. The dialkyl was recovered in high yield from these reactions.

(4.B) Hexakis(trimethylphosphine)bis-μ-methylene-μ-methyldiruthenium(III)-(Ru-Ru) tetrafluoroborate

Fluoroboric acid (0.4 ml, of 43% aqueous solution, 1.9 mmol) in tetrahydrofuran (10 cm^3) was added slowly (2 min) to a solution of (4.A) (1.36 g, 1.9 mmol) in THF (35 cm^3) at room temperature. The mixture was rapidly stirred ($\frac{1}{2}$ h) and the dark red solid was allowed to settle. This was collected, washed with THF (2 x 50 cm^3) and petroleum (50 cm^3) and dried under vacuum. This residue was dissolved in methanol (30 cm^3), filtered and evaporated to ca. 10 cm^3. The solution was warmed briefly (50° C) to ensure complete dissolution then cooled (-20° C) to yield dark red crystals which were collected, washed with THF (10 cm^3) and petroleum (10 cm^3) and dried under vacuum. Yield: 1.4 g, 90%, m.p. 300-20° C dec.

I.r. (Nujol): 1455s, 1445m, 1435w, 1370m, 1310m, 1290m, 1278w,

1060sbr, 1045ssh, 954sbr, 940ssh, 855w, 850w, 725m, 715m, 670m, cm^{-1}. I.r. in fluorocarbon Voltalef 3S (B.D.H.), 2970w, 2908m, 2880w, cm^{-1}.

The compound is soluble in nitromethane, acetonitrile, acetone and methanol although heating in $MeNO_2$ (60° C) for several hours results in some decomposition. It is insoluble in hydrocarbons, THF and diethyl ether and decomposes in $CH_2C\ell_2$ and $CHC\ell_3$ after ca. ½ h although it is stable in $CH_2C\ell_2$ at -80° C for prolonged periods.

It reacts with excess MeLi in THF to give (4.A) in good yield although the reaction in Et_2O is very slow (days).

(4.C) Hexakis(trimethylphosphine)bis-μ-methylenediruthenium(III)(Ru-Ru) bis tetrafluoroborate

Fluoroboric acid (0.58 ml, 43% aqueous solution, 2.8 mmol) in THF (10 cm^3) was added to a solution of (4.A) (1.0 g, 1.4 mmol) in THF (40 cm^3) at room temperature.

The mixture was rapidly stirred (3 h). The orange solid was allowed to settle, collected, washed with THF (2 x 50 cm^3) and petroleum (50 cm^3), and dried under vacuum. It was recrystallised from methanol (as for (4.B)) washed with THF (10 cm^3) and petroleum (10 cm^3) and dried under vacuum. Yield: 1.1 g, 80%, m.p. 240-5° C.

I.r. (Nujol) : 1445s, 1425m, 1365m, 1315w, 1309m, 1291m, 1288m, 1280w, 1090s, 1050sbr, 1038ssh, 987w, 945s, 854w, 765w, 720m, 686w, 670w, 517w, 445w, 400w, cm^{-1}. The compound has similar solubility properties to those of (4.B) but is insoluble in $CH_2C\ell_2$.

(4.D) Hexakis(trimethylphosphine)bis-μ-methylenediruthenium(III)(Ru-Ru) bis(trifluoromethane sulphonate)

This was prepared using a procedure similar to that for (4.C). It was recrystallised from methanol, and dried under vacuum. Yield, ca.

80%, m.p. 203-207° C (dec.).

I.r. (Nujol) : 1450s, 1320m, 1310m, 1308m, 1295m, 1288m, 1270sbr, 1214m, 1145s, 1035s, 950sbr, 860m, 752w, 723m, 685w, 675m, 639s, 573w, 520m, cm^{-1}.

Table 4.1

Analytical Data for Methylene Bridged Ruthenium Compounds

Compound	Colour	Found % [a]			Required %			Λ_M [b]
		C	H	P	C	H	P	
(4.A) $Ru_2(CH_2)_3(PMe_3)_6$	Orange Red	36.5	8.7	27.0	36.0	8.6	26.6	-
(4.B) $[Ru_2(CH_3)(CH_2)_2(PMe_3)_6]BF_4$	Dark Red	31.8	7.7	24.0	32.0	7.7	23.6	95 [c]
(4.C) $[Ru_2(CH_2)_2(PMe_3)_6](BF_4)_2$	Orange	27.9	7.1	23.8	27.9	6.7	21.6	151 [d]
(4.D) $[Ru_2(CH_2)_2(PMe_3)_6](CF_3SO_3)_2$	Orange	27.1	6.1	19.6	26.8	5.9	18.9	163 [e]

[a] M cryoscopic in C_6H_6, found 690 (required 700).

[b] In $MeNO_2$ at 25° C, values in $\Lambda^{-1}cm^2mol^{-1}$.

[c] at 9.0×10^{-4} M.

[d] at 7.8×10^{-4} M.

[e] at 8.0×10^{-4} M.

Table 4.2. ^{1}H and ^{13}C N.M.R. Data for Methylene Bridged Ru(III) Compounds

Compound	^{1}H; δ values [a]				Assignment	$^{13}C\{^{1}H\}$ [b]			
(4.A) $Ru_2(CH_2)_3(PMe_3)_6$	5.22	bt	(6)	$^{3}J_{^{31}P-^{1}H}$ = 15 Hz	Ru-CH_2-Ru	131.26[c]	tt	$^{2}J_{^{13}C-^{31}P}$ = 45.4, 5.1 Hz	
	1.42	t[d]	(54)	$J_{^{31}P-^{1}H}$ = 5 Hz	PMe_3	24.40[d]	t	$J_{^{13}C-^{31}P}$ = 7.1 Hz	
(4.B) $[Ru_2(CH_3)(CH_2)_2(PMe_3)_6](BF_4)$	7.07[ef]	t	(4)	$^{3}J_{^{31}P-^{1}H}$ = 6 Hz	Ru-CH_2-Ru	147.6	bs [fg]		
						148.5	bs	(-80° C) [h]	
	1.4	bs	(54)		PMe_3	16.0	d	$J_{^{13}C-^{31}P}$ = 26.0 Hz	
						20.8	s [i]		(-80°C)
						18.9	d	$J_{^{13}C-^{31}P}$ = 26.2 Hz	
	-5.65	pent	(3)	$^{2}J_{^{31}P-^{1}H}$ = 2 Hz	Ru-CH_3-Ru	-27.1	bs		
(4.C) $[Ru_2(CH_2)_2(PMe_3)_6](BF_4)_2$	8.41[f]	pent	(4)	$^{3}J_{^{31}P-^{1}H} \simeq$ 3.5 Hz	Ru-CH_2-Ru	139.3	s		
	1.3	bs	(54)		PMe_3	16.0	d	$J_{^{13}C-^{31}P}$ = 30.9 Hz	
(4.D) $[Ru_2(CH_2)_2(PMe_3)_6](CF_3SO_3)_2$	7.39[f]	m	(4)		Ru-CH_2-Ru				
	1.44	bs	(54)		PMe_3				

Footnotes - Table 4.2

[a] In C_6D_6 with Me_4Si as internal reference, referenced to Me_4Si (δ 0.0) at 60 MHz and 35° C or at 100 MHz and 28° C. Relative intensity ( ), b = broad, pent = pentuplet.

[b] In C_6D_6 as internal reference (δ 128.7), referenced to Me_4Si (δ 0.0) at 25.2 MHz at 28° C. Peaks to high frequency of Me_4Si are positive.

[c] Partially obscured by solvent resonances.

[d] A 1 : 1 : 1 triplet.

[e] See text.

[f] In CD_3NO_2, with Me_4Si as external reference (^1H). Referenced to Me_4Si (δ 0.0) at δ 57.3 ($^{13}C\{^1H\}$).

[g] This resonance could be a poorly resolved quartet with $^2J_{^{31}P-^{13}C} \approx 3$ Hz.

[h] In $CD_2C\ell_2$ referenced to Me_4Si at δ 53.0.

[i] Relative intensity s : d = 2 : 1.

Table 4.3

$^{31}P\{^{1}H\}$ N.M.R. Spectra of Ruthenium Compounds

	δ values [a]
(4.A) $Ru_2(CH_2)_3(PMe_3)_6$	-14.15 s
(4.B) $[Ru_2(CH_3)(CH_2)_2(PMe_3)_6](BF_4)$	-12.0[b] b -8.0[b] s (65° C) 3.4[c] bs (-80° C) -13.0 t J_{P-P} = 12.1 Hz
(4.C) $[Ru_2(CH_2)_2(PMe_3)_6](BF_4)_2$	-14.1[b] b

[a] In benzene + 10% C_6D_6, referenced to external 85% H_3PO_4 (δ 0.0) at 40.5 MHz. Peaks to high frequency of reference are positive.

[b] In $MeNO_2$ / 10% C_6D_6.

[c] In $CH_2C\ell_2$ / 10% C_6D_6 at -80° C.

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