ORGANOMETALLIC COMPOUNDS OF PLATINUM GROUP METALS

A thesis submitted by

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ABSTRACT

The interaction of various dimeric acetates of the platinum metals as well as the trimeric $[Pd(O_2CMe)_2]_3$ with alkylating agents in both the presence and the absence of phosphines has been studied.

Using $Ru_2(O_2CMe)_4Cl$ the reaction with alkylating agents in the absence of phosphines gives, under certain conditions, compounds of the general formula Ru_2R_6 (where R = CH_2SiMe_3, CH_2CMe_3). These compounds represent the first neutral stable homoleptic alkyls of the platinum metals, and also the first structurally characterised compounds containing triple ruthenium-ruthenium bonds. These studies also produced the previously unknown dirutheniumtetraacetate, the catalytic activity of this compound towards olefin hydrogenation has been investigated.

With $Os_2(O_2CMe)_4Cl_2$ analogous reactions give the partially alkylated product $Os_2(O_2CMe)_2R_4$, these can be further reacted to give $Os_2(\eta^3C_3H_5)_2R_4$. The reaction of $Os_2(O_2CMe)_4Cl_2$ with cyclohexyl Grignard gives tetrahedral $Os(cyclohexyl)_4$, the first mononuclear homoleptic alkyl of the platinum metals. X-ray crystal structures have been obtained of all the above named compounds with the exception of $Os_2(O_2CMe)_2R_4$.

The reaction chemistry of these compounds has been studied. The ruthenium alkyls react with molecular oxygen to give a dimeric oxo alkyl $(RuOR_3)_2$ which has been studied by x-ray crystallography. The reactivity and potential utility of this compound is discussed.

The interactions of the acetates of Ru, Rh and Pd with alkylating agents in the presence of 1,2 bis(dimethylphosphino)ethane, (and also trimethylphosphine for palladium) has been studied. These reactions produce a range of new alkyl phosphine complexes.

CONTENTS

Abstract 2

Contents 3

List of Figures 4

List of Tables 5

Abbreviations 6

Acknowledgements 7

Dedication 8

Introduction 9

Chapter 1 - Ruthenium Alkyls 13

Introduction 14

Results and Discussion 15

Chapter 2 - Osmium Alkyls 31

Introduction 32

Results and Discussion 32

Chapter 3 - Reactions of the Ruthenium Alkyls 50

Reaction with Phosphines 51

Reaction with Oxygen 55

Miscellaneous Reactions 74

Chapter 4 - Diruthenium Tetraacetate 78

Discussion 79

Catalysis 87

Chapter 5 - Palladium, Ruthenium and Rhodium Alkyls 90

Palladium Compounds 97

Ruthenium Compounds 106

Rhodium Compounds 108

Experimental 118

References 135

LIST OF FIGURES.

1. Molecular structure of $Ru_2(CH_2CMe_3)_6$ 16
2. Molecular structure of $Ru_2(CH_2SiMe_3)_6$ 22
3. Reaction scheme for $Ru_2(O_2CMe)_4Cl$ 25
4. $^{13}C['H]$ n.m.r spectrum of $Os_2(O_2CMe)_2(CH_2CMe_3)_4$ 33
5. Molecular structure of $Os_2(\eta^3C_3H_5)_2(CH_2CMe_3)_4$ 37,38
6. Molecular structure of $Os(C_6H_{11})_4$ 45
7. Molecular structure of $Ru_2O_2(CH_2SiMe_3)_6$ 58
8. Interaction of $Ru_2O_2R_6$ with propene..... 68
9. Molecular structure of $Ru_2(O_2CMe)_4 \cdot 2thf$..... 81
10. Electronic configuration of $Ru_2(O_2CH)_4^{n+}$, n=0,1..... 84
11. H_2 uptake by alkenes in presence of $Ru_2(O_2CMe)_4$ 91
12. Change of electronic spectrum of $Ru_2(O_2CMe)_4$ on addition of H_2 92
13. Change of electronic spectrum of $Ru_2(O_2CMe)_4$ on addition of alkene..... 93
14. Effect of tetragonal distortion on metal d orbitals..... 102
15. $^{31}P['H]$ n.m.r spectrum of $Rh_2R_2P_3$ species..... 114

LIST OF TABLES

1. N.m.r data for the ruthenium alkyls..... 28
2. Analytical data for the ruthenium alkyls..... 29
3. Bond angles and lengths for $Ru_2(CH_2CMe_3)_6$ 18
4. Bond angles and lengths for $Ru_2(CH_2SiMe_3)_6$ 23
5. N.m.r data for osmium alkyls..... 48
6. Analytical data for osmium alkyls..... 49
7. Bond angles and lengths for $Os_2(nC_3H_5)_2(CH_2CMe_3)_4$ 39
8. Bond angles and lengths for $Os(C_6H_{11})_4$ 46
9. Bond angles and lengths for $Ru_2O_2(CH_2SiMe_3)_6$ 59
10. Bond angles and lengths for $Ru_2(O_2CMe)_4 \cdot 2thf$..... 82
11. Cyclic voltammetry studies of $Ru_2(O_2CMe)_4$..... 86
12. Hydrogenation studies using $Ru_2(O_2CMe)_4$ 89
13. N.m.r data for the palladium alkyls..... 103,104
14. Analytical data for the palladium alkyls..... 105
15. N.m.r data for ruthenium and rhodium phosphine alkyls..... 115,116
16. Analytical data for the ruthenium and rhodium phosphine alkyls..... 117

ABBREVIATIONS.

atm	101 325 Nm^{-2}
B.M	Bohr Magnetons ($0.927 \times 10^{-23} Am^2$)
b.p.	boiling point
^tBu	CMe_3
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
E.P.R	Electron paramagnetic resonance
Et	CH_2CH_3
eV	electron volt
hν	photolysis
i.r	infra-red
Me	CH_3
μeff	effective magnetic moment
m.p	melting point
n.m.r	nuclear magnetic resonance
PMe_3	trimethylphosphine
p.p.m	parts per million
thf	tetrahydrofuran

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DEDICATED TO MY FAMILY AND

THE MEMORY OF MY FATHER

INTRODUCTION

Organometallic chemistry is a border area between the classical subdivisions of inorganic and organic chemistry. As such it has benefitted from and contributed to advances in both.

Whilst generally considered much younger than the other two branches, the first organometallic compound, tetramethyldiarsine was synthesized, albeit unintentionally as long ago as 1760 by Cadet de Gassincourt (1), a Parisien apothecary. However this was an isolated result whose significance was not realised at the time.

The true beginning can be traced back to the isolation of zinc alkyls by Frankland in 1849 (2). This provoked much interest and led to the isolation of other such compounds for example of mercury (3), tin (3) and lead (4). It was the realisation of the potential synthetic utility of the zinc and magnesium alkyls (the latter prepared by Grignard (5)) that laid the foundations of modern organometallic chemistry.

Within the broader area of organometallic chemistry the emergence of compounds containing bonds between transition metals and carbon is much more recent. Although once again isolated compounds precede the real beginning, (as exemplified by Zeise's salt (1827) (6), trimethyl platinum iodide, synthesized by Pope and Peachy (1909)(7) and Heins' ill characterised polyphenylchromium (1919)(8)), the true starting point for modern organotransition metal chemistry and probably the most significant single event for the whole of organometallic chemistry was the isolation and characterization of the metallocenes.(9) These compounds caught the imagination and led directly to the huge

expansion of the field.

This expansion has been due not only to interest in the synthesis, structure and bonding of these compounds but also because of their widespread use in affecting organic transformations both as stoichiometric reagents and catalysts.

One significant difference exists between the development of the organic chemistry of main group and transition metals, for the former it was almost exclusively the peralkyls (mR_n) which were isolated first (often due to their high volatility). This is not true for the transition metals, where early attempts to prepare pure alkyls failed.

This failure generated a serious misconception that hampered the development of the field, namely that transition metal to carbon bonds are weak and because of this such compounds are intrinsically thermodynamically unstable, only being isolable in the presence of ancillary ligands. Eventually it was realised (10) that this was not so, and it was kinetic instability that led to decomposition. This can be prevented by careful choice of alkyl group, metal oxidation state, other ligands or coordination number and geometry.

Despite this increased understanding of the factors affecting the stability of organotransition metal compounds previous to the work described in this thesis there were no examples of stable neutral per alkyls (homoleptic alkyls) of the platinum group metals (there were a couple of highly unstable anionic ones such as $PtMe_4^{2-}$, (11)).

The recent massive expansion of organometallic chemistry has been matched, in speed, if not yet in scale by that of compounds containing metal-metal bonds. Such compounds have become the focus of intense interest with regard to their electronic and geometric structure and their use in synthesis and catalysis.

As is true of organometallic chemistry, compounds containing metal-metal multiple bonds have been in existence for a long time, chromium (II) acetate which contains a quadruple metal-metal bond was first prepared in 1844 (12)(it was only fully structurally characterised as recently as 1970 (13)). Other compounds synthesized in the early part of this century (such as $Ta_6Cl_{14}\cdot 7H_2O$ (14)) could not be rationalized in classical Wernerian terms, i.e. as a central metal ion surrounded by a discrete set of ligands. Such compounds, which were subsequently shown to contain metal-metal bonds were at the time dismissed as oddities.

The development of this field has gone hand in hand with the increasing sophistication of x-ray diffraction methods and computing techniques in general. It was only after the recognition of double (15) and quadruple bonds (16) between rhenium ions in 1963-64 using x-ray analysis that the rapid expansion began.

Since then multiple bonds of various orders have been characterised and studied in detail for many of the transition elements. Examples of multiple bonds between ruthenium and osmium ions are however noticeably scarce. Thus the compounds described in this thesis not only represent the first stable neutral homoleptic alkyls of the platinum metals, but also the first well characterised examples of Ru-Ru triple bonds and unbridged Os-Os triple bonds.

The latter part of this thesis is concerned with the synthesis and characterization of new alkyl complexes of Ru, Rh and Pd, containing the phosphine ligands, 1,2 bis(dimethylphosphino)ethane (dmpe) or for one group trimethylphosphine (PMe_3). The placement of these compounds after the peralkyl compound is in direct contrast to the chronological order in which they were made, but the author feels this reflects the relative interest and significance of the pieces of work.

CHAPTER 1

DIMERIC RUTHENIUM (III) ALKYLS

DIMERIC RUTHENIUM (III) ALKYLS

INTRODUCTION

The interaction of alkylating agents with binuclear transition metal acetates $M_2(OCR)_4^{n+}$ (n = 0, 1 or 2, M = Cr, Mo, Rh, Ru, Os, Pd) has generally only given isolable products in the presence of phosphines (17). The only exeptions being those between dimolybdenum (II) tetraacetate and methyl lithium (18) and between dichromium (II) tetraacetate and dirhenium (III) tetraacetate dichloride and a range of alkylating agents (19).

It has previously been reported(20) that in the absence of phosphines alkylations of dirhodium (II) tetraacetate or dichromium (II) tetraacetate led to decomposition, no mention was made of diruthenium tetraacetatechloride (from now on referred to as rutheniumacetate chloride, $Ru_2(O_2CMe)_4Cl$).

These ruthenium tetracarboxylate species were first prepared by refluxing commercial hydrated ruthenium (III) chloride in carboxylic acid - anhydride mixtures(21). The method used to prepare them for present studies followed a later improved method(22). Structural studies of the propionate showed them to exist as $Ru_2(O_2CR)_4^+$ units linked into infinite chains by chloride ions. This repeat unit means that despite the conventional formula $Ru_2(O_2CR)_4Cl$ the ruthenium ions are equivalent and should be assigned the same net oxidation state of +2.5, (more will be said about the electronic structure of these compounds in chapter 4). The ruthenium-ruthenium distance of 2.28 Å is indicative of a strong metal-metal bond.

As mentioned in the introduction it is possible to stabilize organometallic compounds by careful choice of alkyl group. Since one of the most facile decomposition routes proceeds via β-hydride elimination (23) absence of such hydrogens in the alkyl group is obviously advantageous. Such alkyl groups are commonly known as elimination stabilized, the two most widely used in this thesis are trimethylsilylmethyl $(CH_3)_3Si\ CH_2$ - and neopentyl $(CH_3)_3$-C-CH_2-. These groups have been widely used elsewhere.

DISCUSSION

The first reaction attempted was that between ruthenium acetate chloride and Me_3C-CH_2MgCl in tetrahydrofuran (thf) at low temperature. Extraction of the reaction residues with hexane gives a purple solution from which purple prisms of hexakis(neopentyl) diruthenium (III) $Ru_2(CH_2CMe_3)_6$ can be isolated.

The i.r. spectrum of this compound is largely uninformative comprising only of normal neopentyl resonances which are well documented, the sole diagnostic feature being the absence of acetate bands.

The n.m.r. spectra are also very simple, the ^1H n.m.r. spectrum consists of two sharp singlets at δ+2.81 and δ+1.15 with intensities in the ratio 2:9, obviously due to the neopentyl methylene ($-CH_2-$) and methyl ($-CH_3$) protons respectively. The $^{13}C[^1H]$ spectrum contains three sharp singlets at δ+51.7, δ+33.1 and δ+31.6. The spectroscopic data for this and the other ruthenium alkyls are collected in Table 1, the analytical data for these compounds are collected in Table 2. The compound was sufficiently stable and volatile to give a mass spectrum, m/e = 628.

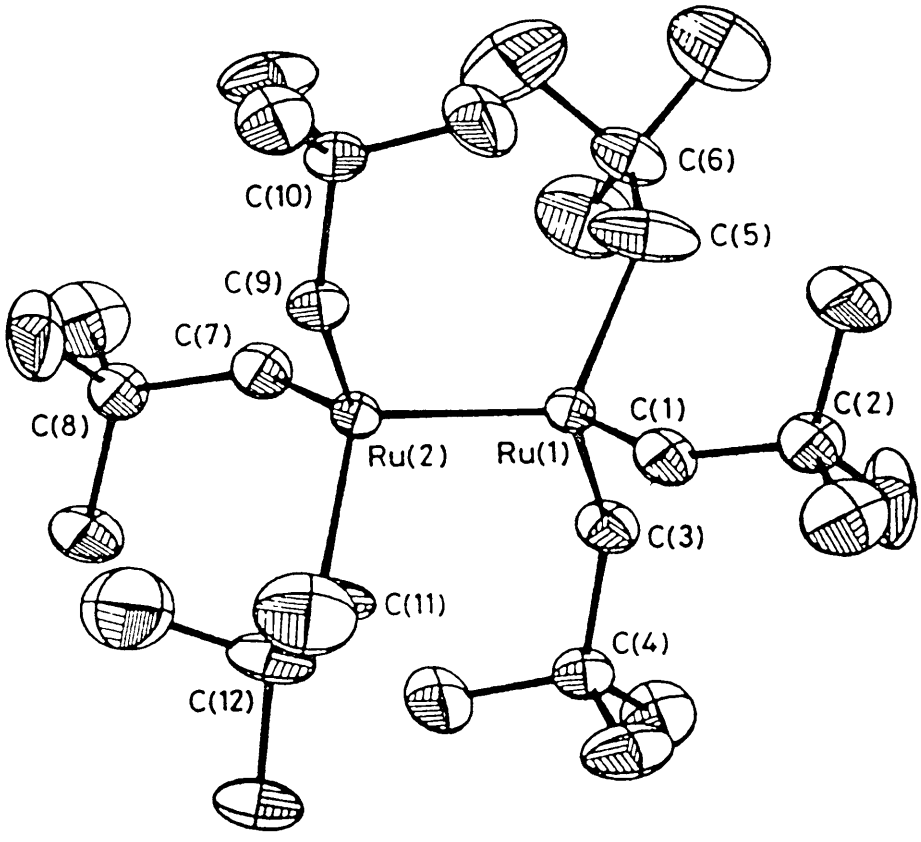


FIGURE 1: MOLECULAR STRUCTURE OF $Ru_2(CH_2CMe_3)_6$

The compound has been fully characterised by an x-ray structure determination. The molecule has an R_3MMR_3 ethane like structure in which the MR_3 groups are staggered giving D_3 symmetry (Figure 1). Although not isoelectronic, the structure of this molecule is thus similar to those of $M_2(CH_2SiMe_3)_6$ (24), $M_2(NR_2)_6$ (25) and $M_2(OR)_6$ (26), M = Mo, W. The geometry around each ruthenium is approximately tetrahedral, the angles between the neopentyl ligands around the metal centre lie in the range 102-118°.

The compound can be considered as a derivative of the triply bonded Ru_2^{6+} core in which the ten electrons not involved in ligand bonding are distributed amongst the molecular orbitals as $\sigma^2\pi^4\delta^2\delta^{*2}$, this is consistent with the observed diamagnetism of the compound. Unexpectedly the Ru-Ru bond length of 2.311 Å is longer than that found in the Ru_2^{5+} carboxylates (2.250-2.290 Å), which have a formal bond order of 2.5 (compared with 3 in this alkyl compound). This serves to emphasise that bond order is a qualitative concept and bond length is sensitive to factors other than electronic configuration. Important bond lengths and angles are collected in Table 3.

This compound was the first to contain a Ru-Ru triple bond of any kind, since its isolation a compound containing a bridged triple bond has been reported (27), but there are still no other examples of such unsupported bonds. The only other compound containing a Ru_2^{6+} core namely $Ru_2L_2^{2+}$ (L = tetraaza(14)annulene) has not been fully characterised (28).

TABLE 3 SELECTED BOND LENGTHS AND BOND ANGLES FOR $Ru_2(CH_2CMe_3)_6$

Ru(2)-Ru(1)	2.311(3)	C(1)-Ru(1)	2.033(7)
C(3)-Ru(1)	2.033(8)	C(5)-Ru(1)	2.043(8)
C(7)-Ru(2)	2.031(8)	C(9)-Ru(2)	2.021(8)
C(11)-Ru(2)	2.052(8)		
C(2)-C(1)	1.523(11)		
C(4)-C(3)	1.538(9)		
C(6)-C(5)	1.478(9)		
C(8)-C(7)	1.523(10)		
C(10)-C(9)	1.540(9)		
C(12)-C(11)	1.433(10)		
C(1)-Ru(1)-Ru(2)	101.8(3)	C(3)-Ru(1)-Ru(2)	114.4(3)
C(3)-Ru(1)-C(1)	115.4(3)	C(3)-Ru(1)-Ru(2)	117.5(4)
C(5)-Ru(1)-C(1)	106.5(4)	C(5)-Ru(1)-C(3)	101.6(4)
C(7)-Ru(2)-Ru(1)	101.3(3)	C(9)-Ru(2)-Ru(1)	115.1(3)
C(9)-Ru(2)-C(7)	117.9(3)	C(11)-Ru(2)-Ru(1)	106.4(4)
C(11)-Ru(2)-C(7)	113.2(4)	C(11)-Ru(2)-C(9)	102.8(4)
C(2)-C(1)-Ru(1)	125.3(5)		
C(4)-C(3)-Ru(1)	129.5(5)		
C(6)-C(5)-Ru(1)	133.4(5)		
C(8)-C(7)-Ru(2)	126.6(5)		
C(10)-C(9)-Ru(2)	128.6(5)		
C(12)-C(11)-Ru(2)	135.6(5)		

Originally the mechanism of formation of the alkylated products was unknown, the apparent reaction stoichiometry was

$$Ru_2^{5+} + 6\ RMgX \longrightarrow Ru_2^{6+}$$

Thus, formally oxidation had ocurred, but the source or identity of the oxidising agent was unknown. In addition to carrying out the reactions under strictly anaerobic conditions, rigorous attempts were made to exclude any other oxidants such as peroxides in the solvents and impurities in the starting materials, but this had no effect on the yield of the Ru_2^{6+} product. At the other extreme no improvement of yield was observed when external oxidants such as bis ^{t}butylperoxide were added. This seemed to indicate that the source of oxidation was either one or both of the reactants rather than a trace impurity.

Two further points are worthy of note, first the yields were always less than 50%, and secondly that there were large amounts of reaction residues remaining after the removal of the alkylated products. This led to speculation that a disproportionation reaction was occuring.

Additional evidence for this was obtained from the reaction of ruthenium acetate chloride with Me_3SiCH_2MgCl in thf, when the only product isolated is diruthenium(II)tetraacetate bistetrahydrofuran, $Ru_2(O_2CMe)_4 \cdot 2$ thf. This is formally a Ru_2^{4+} compound, and as such was potentially the other product in a disproportionation reaction involving Ru_2^{5+} and Ru_2^{6+} species. In this case however as it was the only isolable product, this did not represent unequivocal evidence for the disproportionation mechanism, but rather showed that reduction as well as oxidation

could occur during alkylation reactions.

The necessary proof was obtained by careful work up of the reaction residues from the neopentyl reaction. Following the removal of the alkylated product by extraction with hexane, addition of coordinating solvents such as thf or acetonitrile gives coloured solutions from which diruthenium tetraacetate can be isolated. Thus the reaction equation is

$$2\ Ru_2^{5+} \longrightarrow Ru_2^{6+} + Ru_2^{4+}$$

Presumably in the case of the trimethylsilylmethyl reaction in thf, the alkylated product does form initially but is not stable, this is confirmed by the observation that crystalline samples of hexakis(trimethylsilylmethyl)ruthenium(III) (see later) decompose in thf at room temperature in less than half an hour.

Initially attempts to prepare analogous compounds were unsuccessful, the reaction with neophyl Grignard reagent, $PhMe_2C\ CH_2\ MgCl$ gives an intractable red oil. This oil is highly air and moisture sensitive and highly soluble in hydrocarbons. It freezes at approximately 0^oC, and will not distill or sublime even under vacuum. Attempts to purify it using column chromatography on silica or alumina led to decomposition, other columns such as Sephadex failed to effect any separation.

The proton n.m.r spectrum indicates the presence of more than one compound, probable impurities are organic species, witnessed to by high carbon and hydrogen elemental analyses results.

As mentioned above the reaction between ruthenium acetate chloride and Me_3SiCH_2MgCl in thf gives only the reduced Ru_2^{4+} species, however the same reaction in diethyl ether gives blue-green hexakis(trimethylsilylmethyl)diruthenium(III) in 30% yield. This hexane soluble compound is very air and moisture sensitive, much more so than the neopentyl analogue, being pyrophoric as a solid. Because of this great care must be taken during preparation traces of thf cause decomposition and only the tetraacetate can be isolated, similarly impurities in either of the starting materials cause the reaction to fail.

As before the i.r spectrum is largely uninformative and the ^1H n.m.r. spectrum is very simple showing two singlets at δ + 1.51 and δ + 0.21 ppm, with relative intensities 2:9, due to the methylene and methyl protons. The $^{13}C[^1H]$ spectrum consists of two singlets at δ + 15.86 and δ + 1.03 ppm. The parent ion in the mass spectrum occurs at 724.

As expected an x-ray crystallographic study has revealed that the structure of this compound (Figure 2) is very similar to that of $Ru_2(CH_2CMe_3)_6$.

Thus the alkyl ligands are approximately tetrahedrally disposed around the metal centres in a mutually staggered conformation. The Ru-Ru bond length of 2.265(3) Å is slightly shorter than that in the neopentyl analogue. Selected bond lengths and bond angles are collected in Table 4 .

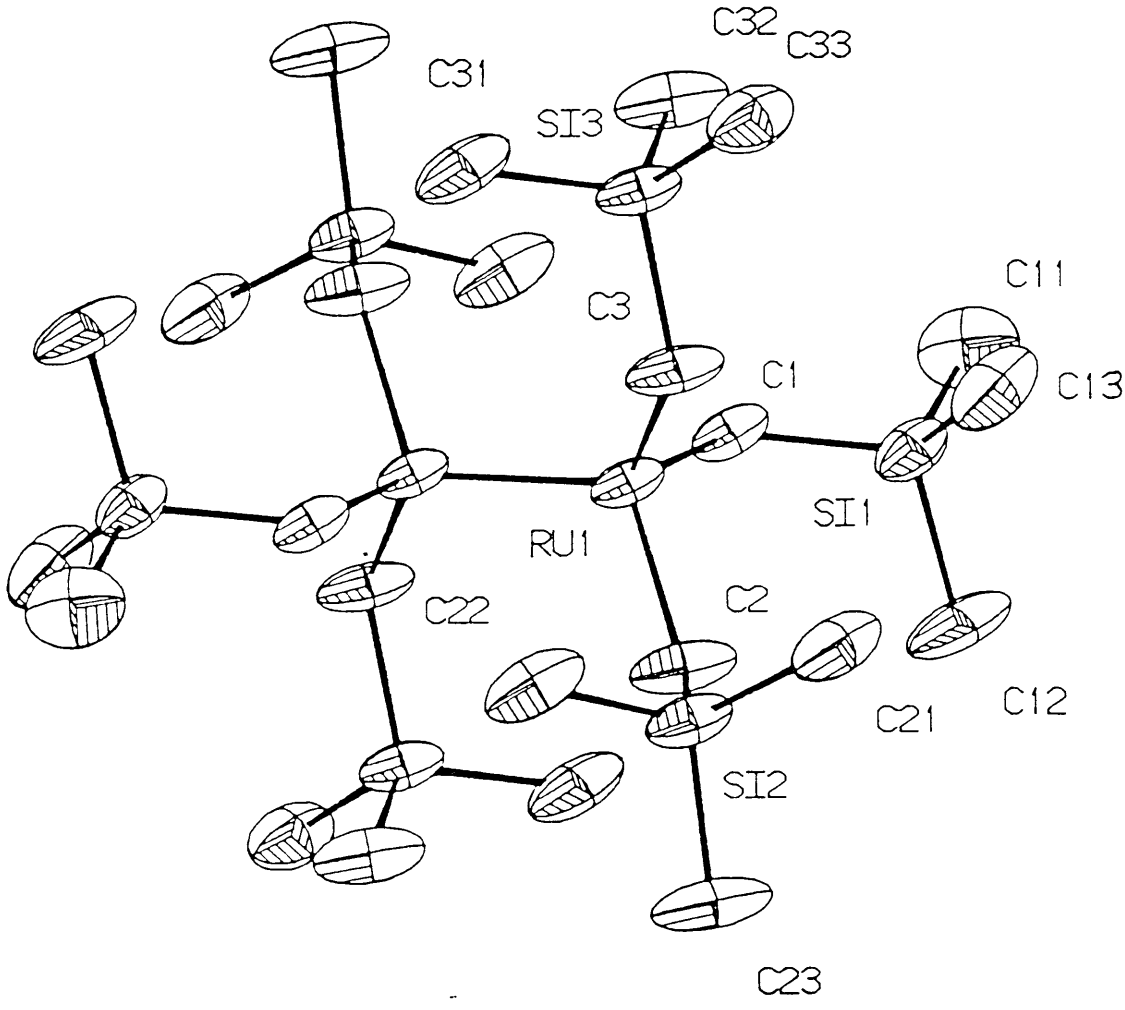


FIGURE 2: MOLECULAR STRUCTURE OF $Ru_2(CH_2SiMe_3)_6$

TABLE 4: SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR $Ru_2(CH_2SiMe_3)_6$

C(1)-Ru(1)	2.021(5)	C(2)-Ru(1)	2.036(5)
C(3)-Ru(1)	2.036(5)	Ru(1)-Ru(1a)	2.265(3)
C(1)-Si(1)	1.870(5)	C(11)-Si(1)	1.872(6)
C(12)-Si(1)	1.869(6)	C(13)-Si(1)	1.867(6)
C(2)-Si(2)	1.871(5)	C(21)-Si(2)	1.869(5)
C(22)-Si(2)	1.874(6)	C(23)-Si(2)	1.880(6)
C(3)-Si(3)	1.869(5)	C(31)-Si(3)	1.865(6)
C(32)-Si(3)	1.878(6)	C(33)-Si(3)	1.880(6)
C(2)-Ru(1)-C(1)	108.6(2)	C(3)-Ru(1)-C(1)	112.8(2)
C(3)-Ru(1)-C(2)	103.5(2)		
Si(1)-C(1)-Ru(1)	121.8(3)	Si(2)-C(2)-Ru(1)	124.7(3)
Si(3)-C(3)-Ru(1)	125.2(3)		
C(11)-Si(1)-C(1)	106.5(3)	C(12)-Si(1)-C(1)	110.9(3)
C(12)-Si(1)-C(11)	108.6(3)	C(13)-Si(1)-C(1)	112.2(3)
C(13)-Si(1)-C(11)	109.5(3)	C(13)-Si(1)-C(12)	109.0(3)
C(21)-Si(2)-C(2)	110.3(3)	C(22)-Si(2)-C(2)	113.9(3)
C(22)-Si(2)-C(21)	109.8(3)	C(23)-Si(2)-C(2)	107.7(3)
C(23)-Si(2)-C(21)	107.7(3)	C(23)-Si(2)-C(22)	107.2(3)
C(31)-Si(3)-C(3)	108.8(3)	C(32)-Si(3)-C(3)	112.7(3)
C(32)-Si(3)-C(31)	111.6(3)	C(33)-Si(3)-C(3)	108.4(3)
C(33)-Si(3)-C(31)	107.5(3)	C(33)-Si(3)-C(32)	107.7(3)

These alkylations can be controlled to give partially alkylated products, thus the reaction of four equivalents of $Me_3C\ CH_2MgCl$ with ruthenium acetate chloride over reduced reaction times gives red crystalline, air sensitive, hexane soluble tetrakis(neopentyl)bis(μ-acetato)diruthenium(III). This compound retains two bridging acetate groups whose presence is indicated in the i.r. spectrum by bands at 1480 and 1563 cm^{-1}, corresponding to the symmetric and asymmetric carboxylate stretches (29). The ^1H n.m.r. spectrum now consists of three sharp singlets at δ + 2.69, δ + 1.71 and δ + 1.28 ppm of relative intensity 8:6:36, obviously corresponding to the neopentyl methylene, the acetate methyl and the neopentyl protons respectively. The $^{13}C[^1H]$ spectrum consists of five sharp singlets, the low field resonance (at δ + 185.70 ppm) is particularly diagnostic of a carboxylic carbon centre, the spectrum can be interpreted with reference to the analogous rhenium system (19e).

A similar reaction with Me_3SiCH_2MgCl in diethyl ether gives tetrakis(trimethylsilylmethyl)bis(μ-acetato)diruthenium(III) in 25% yield. This reaction is much more sensitive to reaction conditions, and should be pumped to dryness to prevent formation of the hexa-alkyl.

Suitable crystals for x-ray diffraction studies could not be obtained for either of these compounds. However the structural assignments can be made confidently on the basis of spectroscopy (n.m.r., i.r), mass spectroscopy, molecular weight and elemental analyses.

The above indicates the range of products available from these

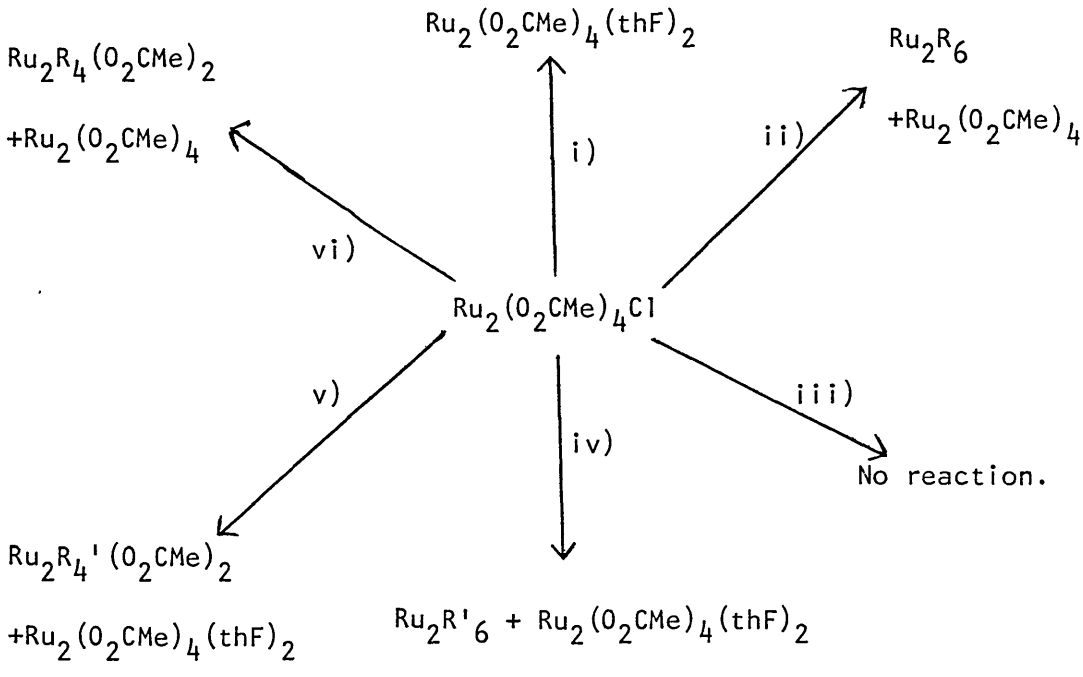


FIGURE 3 : Interaction of $Ru_2(O_2CMe)_4Cl$ with Grignard reagents or dialkylmagnesiums.

$R = CH_2SiMe_3$ $R' = CH_2CMe_3$.

Reactions carried out at -80^oC and allowed to warm to ambient temperature.

i) 4 or 6 equivalents of RMgX in THF.

ii) 6 equivalents of RMgX in diethylether.

iii) 4 or 6 equivalents of R'MgX in diethylether.

iv) 6 equivalents of R'MgX in THF.

v) 4 equivalents of R'MgX in THF.

vi) 4 equivalents of RMgX in diethylether.

reactions, with not all species being isolable under all conditions, the overall reaction scheme is shown in Figure 3.

RUTHENIUM MIXED ALKYLS

The remaining bridging acetate groups in the partially alkylated products can be readily removed by other alkyl groups. Thus the interaction of $Ru_2(O_2CMe)_2(CH_2CMe_3)_4$ with dimethyl magnesium in a mixture of diethyl ether and hexane (1:3) at $-80^{o}C$ gives a deep purple solution when allowed to warm to room temperature, from which dimethyltetrakis(neopentyl)diruthenium(III) can be isolated in greater than 80% yield.

The i.r. spectrum of this air sensitive pink compound indicates the complete removal of the acetate ligands. The ^{1}H n.m.r. is similar to that of the acetate-alkyl compound, consisting of three sharp singlets, with relative intensities of 8:6:36, but whose chemical shift is different. The $^{13}C[^{1}H]$ spectrum shows a new singlet at δ + 18 ppm ; this chemical shift is more indicative of normal terminal methyl groups, in an analogous compound containing bridging methyl groups, these resonances occur at much higher field (δ - 5.65 ppm)(17).

A similar reaction using methyl lithium also in a mixture of hexane and diethyl ether at $-80^{o}C$, gives an immediate bright yellow colour. As it is allowed to warm to room temperature this subsides and is replaced by a purple solution, which eventually yields the same product as above. Attempts to isolate this yellow compound have been unsuccessful, as it decomposes rapidly above $-50^{o}C$ to give a purple solution and

more slowly at lower temperatures over the course of a few hours. It is tempting to postulate this species is some kind of lithium alkylate anion, but there is no evidence available to support this.

A similar reaction using diethylmagnesium gives a pink-purple compound, elemental analysis and spectroscopy indicate the formula $Ru_2(C_2H_5)_2(CH_2CMe_3)_4$. The ^1H n.m.r. shows a triplet at δ + 1.68 with J_{H-H} = 4 Hz and a quartet at δ + 0.51 with similar coupling constants, indicative of the presence of an ethyl group.

The photochemical and thermal rearrangements of this compound, which should prove interesting have not yet been fully elucidated.

TABLE 1. NUCLEAR MAGNETIC RESONANCE DATA FOR THE RUTHENIUM ALKYLS

COMPOUND	CHEMICAL SHIFT, δ /ppm	
	^1H, J(Hz)	$^{13}C[^1H]$
$Ru_2(CH_2CMe_3)_6$	2.81s(12, $\underline{CH_2}CMe_3$)	51.70s($\underline{CH_2}$-CMe_3)
	1.15s(54, $CH_2C\underline{Me_3}$)	33.10s(CH_2-$\underline{C}Me_3$)
		31.60s(CH_2-$C\underline{Me_3}$)
$Ru_2(CH_2SiMe_3)_6$	1.51s(12, $\underline{CH_2}SiMe_3$)	15.86s($\underline{CH_2}$-$SiMe_3$)
	0.21s(54, $CH_2Si\underline{Me_3}$)	1.03s(CH_2-$Si\underline{Me_3}$)
$Ru_2(O_2CMe)_2(CH_2CMe_3)_4$	2.69s(8, $\underline{CH_2}$-CMe_3)	185.70s($O_2\underline{C}Me$)
	1.71s(6, $O_2C\underline{Me}$)	52.60s($\underline{CH_2}$-CMe_3)
	1.28s(36, CH_2-$C\underline{Me_3}$)	33.60s(CH_2-$\underline{C}Me_3$)
		30.10s(CH_2-$C\underline{Me_3}$)
		23.20s($O_2C\underline{Me}$)
$Ru_2(O_2CMe)_2(CH_2SiMe_3)_4$	1.85s(6, $O_2C\underline{Me}$)	180.10s($O_2\underline{C}Me$)
	1.31s(8, $\underline{CH_2}Si(Me)_3$)	22.80s($O_2C\underline{Me}$)
	0.25s(36, $CH_2Si\underline{Me_3}$)	13.40s($\underline{CH_2}SiMe_3$)
		0.80s($CH_2Si\underline{Me_3}$)
$Ru_2Me_2(CH_2CMe_3)_4$	2.75s(8, $\underline{CH_2}CMe_3$)	52.3s($\underline{CH_2}$-CMe_3)
	1.74s(6, $\underline{CH_3}$)	35.8s(CH_2-$\underline{C}Me_3$)
	1.05s(36,CH_2-$C\underline{Me_3}$)	27.4s(CH_2-$C\underline{Me_3}$)
		18.6s(-$\underline{CH_3}$)
$Ru_2Et_2(CH_2CMe_3)_4$	2.86s(8, $\underline{CH_2}CMe_3$)	57.8s($\underline{CH_2}$-CMe_3)

1.68't'(6, $CH_2\underline{CH}_3$)

$\underline{J}_{H-H}$ = 4

1.28s(36, $CH_2-C\underline{Me}_3$)

0.51''q''(4, $\underline{CH}_2-CH_3$),

$\underline{J}_{H-H}$= 4

41.4s($CH_2-\underline{C}Me_3$)

26.3s($CH_2-C\underline{Me}_3$)

18.0s($CH_2-\underline{CH}_3$)

10.3s($\underline{CH}_2-CH_3$)

TABLE 2. ANALYTICAL DATA FOR THE RUTHENIUM ALKYLS.

COMPOUND	COLOUR	m.p. θ/°C	FOUND (required) C	H	O	Si
$Ru_2(CH_2CMe_3)_6$	PURPLE	137d	57.5 (57.3)	10.5 (10.5)	-	-
$Ru_2(CH_2SiMe_3)_6$	GREEN	124d	40.0 (39.7	9.1 (9.1)	-	23.0 (22.7)
$Ru_2(O_2CMe)_2(CH_2CMe_3)_4$	RED	143d	47.7 (47.7)	8.4 (8.3)	10.6 (9.4)	-
$Ru_2(O_2CMe)_2(CH_2SiMe_3)_4$	RED	112	36.0 (35.9)	7.5 (7.5)	10.0 (9.6)	17.1 (16.8)
$Ru_2Me_2(CH_2CMe_3)_4$	PURPLE	178d	51.4 (51.2)	9.4 (9.7)	-	-
$Ru_2Et_2(CH_2CMe_3)_4$	PINK	103d	53.4 (52.9)	10.0 (9.9)	-	-

CHAPTER 2

OSMIUM ALKYL COMPOUNDS

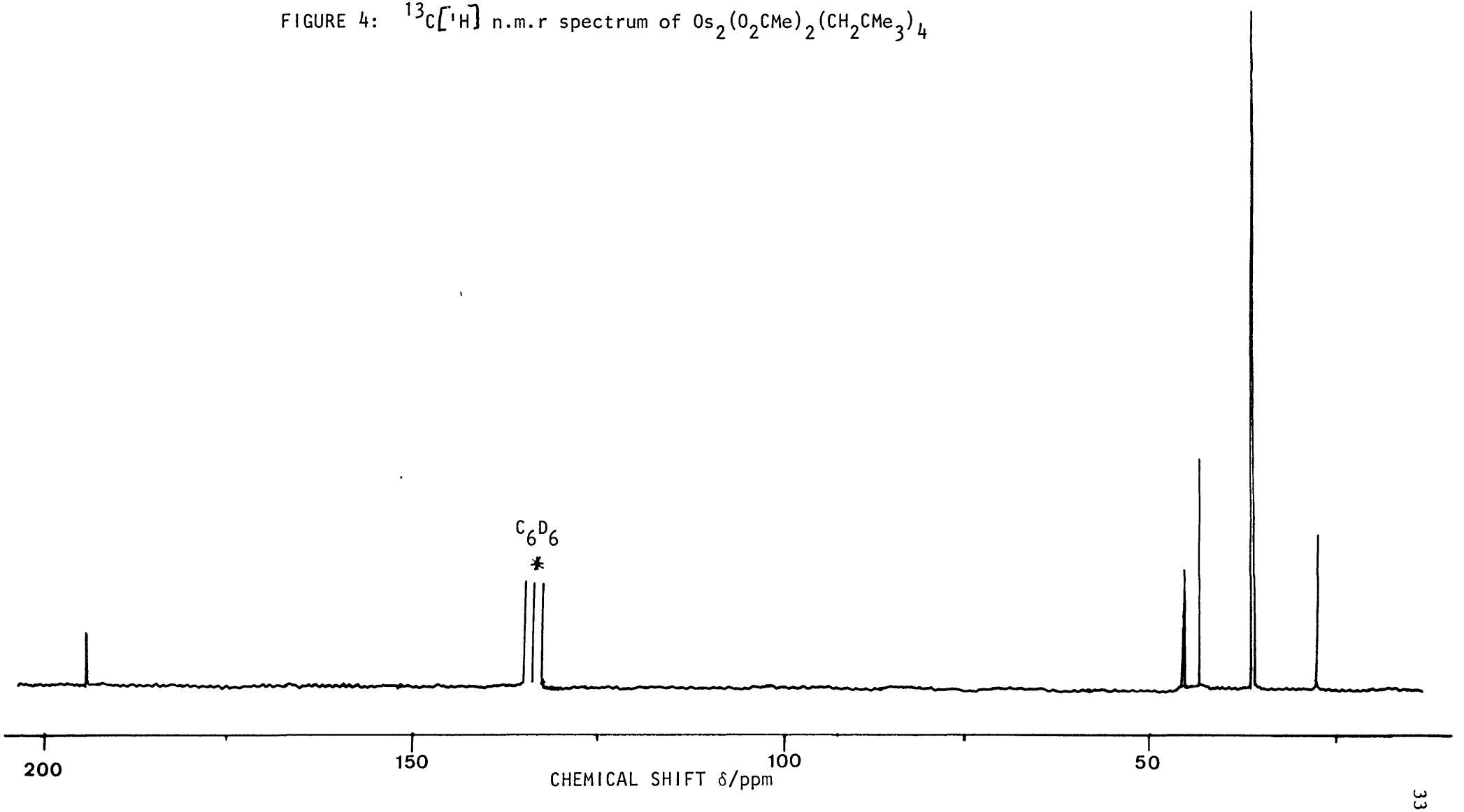
CHAPTER 2 OSMIUM ALKYL COMPOUNDS

Whereas the interaction of alkylating agents with ruthenium acetate chloride can be controlled to give either partially or totally alkylated products, the corresponding reaction with osmium acetate chloride ($Os_2(O_2CMe)_4Cl_2$) yields only the partially alkylated product $Os_2(O_2CMe)_2R_4$ (R= neopentyl or trimethylsilylmethyl), which retains two bridging acetate groups.

The products are highly coloured (olive green for the neopentyl, red for the trimethylsilylmethyl) air sensitive, hexane soluble compounds. Despite their apparent crystallinity both proved to be consistently unsuitable for x-ray crystallography (mainly due to twinning problems) however their structure can be unequivocally assigned on the basis of elemental analyses,i.r and n.m.r spectroscopy. For the neopentyl compound the i.r. spectrum shows two bands at 1540 and 1475 cm^{-1} attributable to the symmetric and asymmetric carboxylate stretches. The ^1H n.m.r. spectrum shows an extra peak due to the acetate methyl protons, in addition to the two singlets from the hydrocarbon ligand. The $^{13}C[^1H]$ spectrum is similar to that of the ruthenium analogue (see previous chapter) showing a low field singlet at δ + 194 ppm. The spectrum of $Os_2(O_2CMe)_2(CH_2CMe_3)_4$ is shown in Figure 4. The data for this and the other osmium alkyls are collected in Tables 5 and 6.

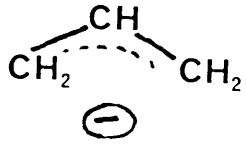
These species are stubbornly resistant to further alkylation. Large excesses of alkylating agent merely lead to faster product formation, this behaviour has been observed previously for $Re_2(O_2CMe)_4Cl_2$ (19e). Reaction of pure samples of $Os_2(O_2CMe)_2R_4$ with simple alkylating agents RLi, R_2Mg, RMgx (R= CH_3,C_2H_5, Me_3SiCH_2.

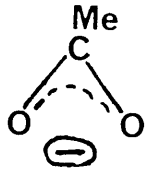
FIGURE 4: $^{13}C[^{1}H]$ n.m.r spectrum of $Os_2(O_2CMe)_2(CH_2CMe_3)_4$



Me_3CCH_2 etc) leads to decomposition in all cases where reaction occurs. Reaction with aryl Grignard reagents was also unsuccessful, often giving intractable metal containing species and the organic dimerization product. This behaviour is exemplified by the reactions with PhMgBr or 2-$MeOC_6H_4MgBr$, which in addition to an unidentified metal species yield biphenyl and 2,8 dimethoxybiphenyl respectively, (these organic compounds were identified by elemental analyses and spectroscopy). The latter aryl reagent was used as it has the ability not only to bond through the aromatic ring carbon, but also via the lone pair on the oxygen and thus exert a further stabilizing influence.

The potential versatility of the bonding modes of the allyl moiety (C_3H_5) made it an attractive reagent for this reaction, particularly since one of its most prevalent forms is as a three centre, three electron, mono anionic donor, which has obvious structural and electronic similarities to the acetate ion.





This form has the proven ability to stabilize metal-metal multiple bonds, both bridging the bond (30) or chelating discrete metal centres (31). The other main coordination mode is as a monodentate, σ-bonded one electron ligand (32).

The reaction between the partially alkylated osmium species and two equivalents of allyl magnesium bromide proceeds rapidly at

-30°C in a mixture of hexane and diethyl ether (5:1)-

$$Os_2(\mu O_2CMe)_2R_4 + 2C_3H_5MgBr \longrightarrow Os_2(\eta^3C_3H_5)_2R_4$$

This orange, air sensitive highly crystalline compound has been characterised by elemental analyses and n.m.r. In addition to the resonances due to the neopentyl ligand the 'H n.m.r spectrum of this compound consists of three sets of signals, a multiplet centred at δ + 3.99 ppm due to the central proton of the allyl moiety, and two doublets at δ + 3.27 ppm (J_{H-H} = 4 Hz) and δ + 1.50 ppm (J_{H-H} = 4 Hz) presumably due to the exo and endo protons. The $^{13}C['H]$ spectrum is very simple, consisting of two sharp singlets at δ + 102 and δ + 46 ppm.

Compounds containing Os-Os triple bonds are scarce. Bridged triple bonds are known where the metal-metal bond is bridged by ligands with O,O (33); O,N (34); P,C (35) and N,N (36) donor sets. This compound was the first to contain an unbridged Os-Os triple bond, very recently another such bond in the compound $Os_2Cl_8^{2-}$ has been brought to our attention (37), and will be referred to later.

The compound $Os_2(\eta C_3H_5)_2(CH_2CMe_3)_4$ forms orange monoclinic crystals and crystallises with two independent but virtually identical molecules in the asymmetric unit, one possesses a centre of symmetry the other does not, but the deviation is minimal.

The x-ray crystallographic study of this compound reveals that the triple bond present in the original starting material

$Os_2(O_2CMe)_4Cl_2$ has not only been retained but strengthened, the Os-Os bond length being 2.197(3) Å as compared to approximately 2.30 Å in the carboxylates. At the time of preparation this was the shortest Os-Os bond known, those in the bridged compounds lie in the range 2.27-2.39 Å , the octachloro derivative however has an even shorter bond, 2.195(2) Å.

The reasons for the remarkably short metal-metal bond are not apparent, but may be in some way connected with the other striking structural feature of the compound, namely the eclipsed geometry adopted by the ligands (Figure 5), this eclipsed stereochemistry is also observed in $Os_2Cl_8^{2-}$.

The two main factors affecting ligand conformation adopted about the metal-metal bond are electronic and steric. In many compounds containing M-M bonds, and most pertinently containing triple bonds the latter seems to be the dominant factor, steric repulsion between ligands ensures that a staggered conformation is observed, examples include $W_2(CH_2SiMe_3)_6$ (24) and $Mo_2(NMe_2)_6$ This steric repulsion is also often reflected by the disposition of atoms in the ligands themselves.

The position is reversed and electronic configuration becomes the dominant factor when the bond order is 3.5 or 4. Here there is a δ bonding component which unlike σ or π orbitals does not possess cylindrical symmetry and whose strength is therefore highly sensitive to rotation about the metal-metal bond.

Between these two extremes there are areas where neither factor is dominant. The eclipsed conformation in this molecule

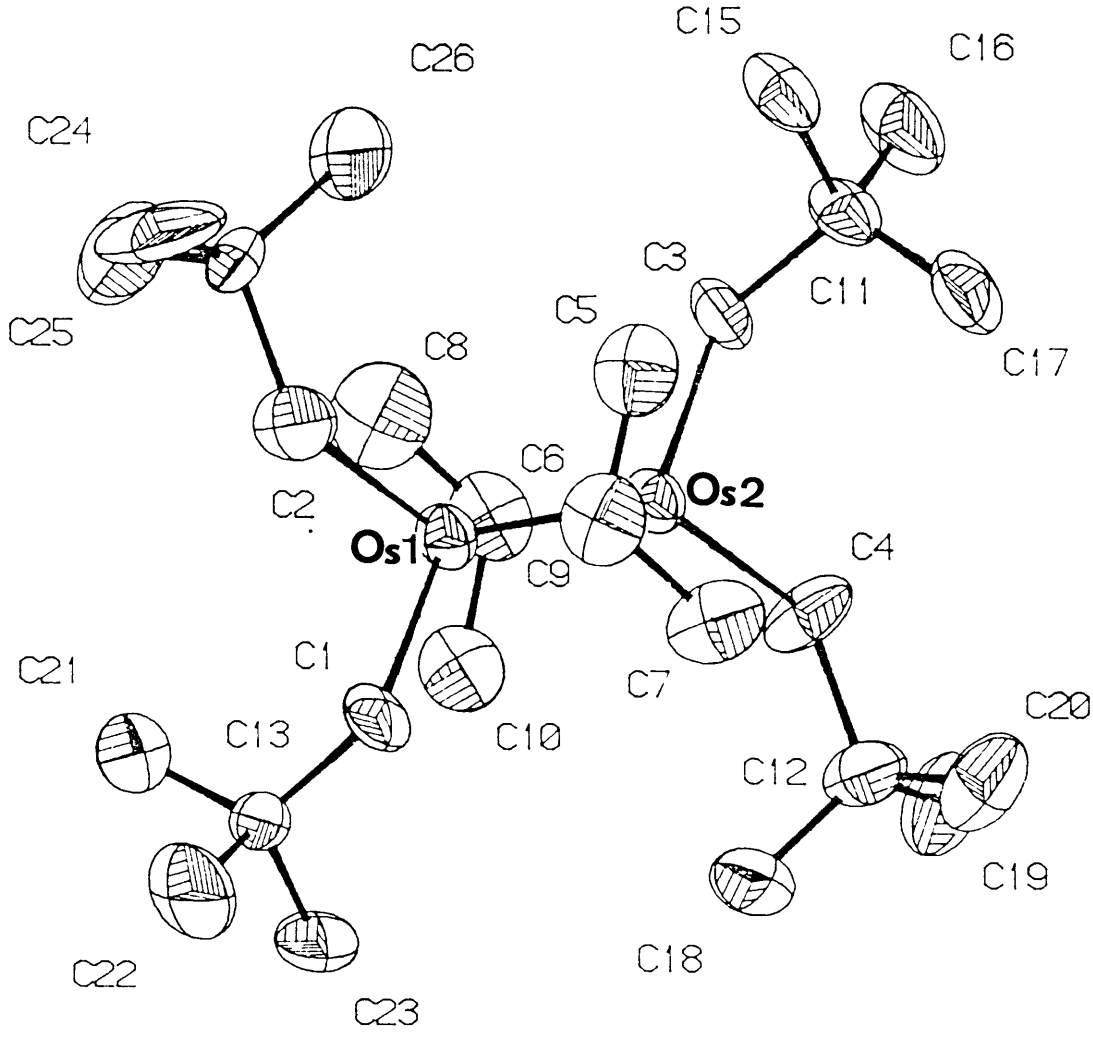


FIGURE 5: MOLECULAR STRUCTURE OF $Os_2(\eta^3C_3H_5)_2(CH_2CMe_3)_4$.

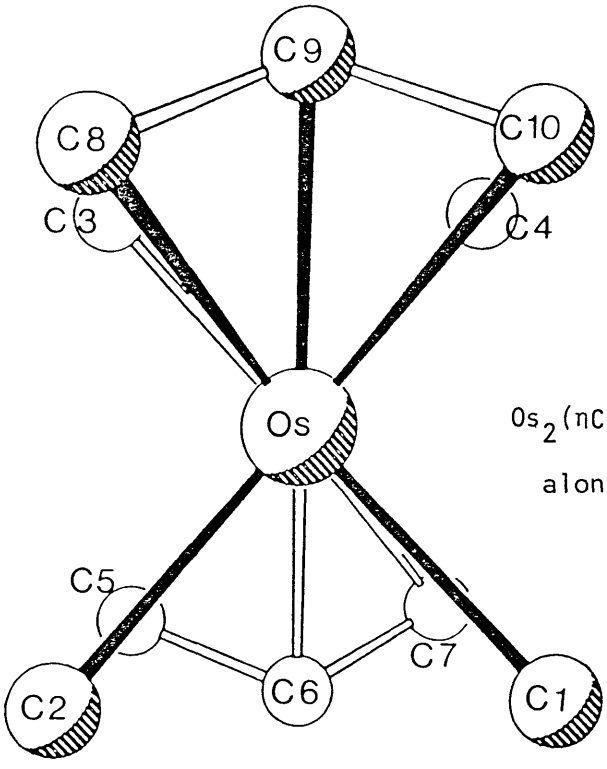


Figure 5a.

View of

$Os_2(nC_3H_5)_2(CH_2CMe_3)_4$

along Os-Os axis.

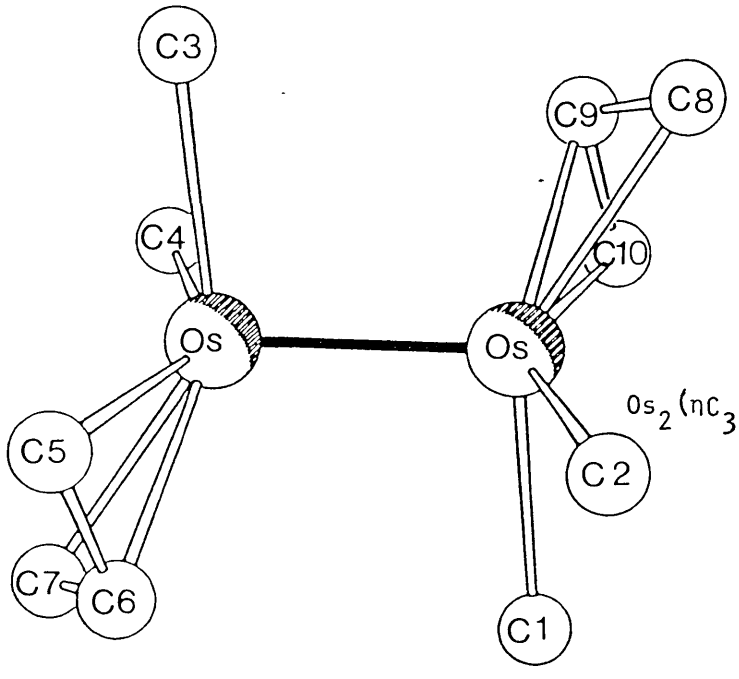


Figure 5b.

$Os_2(nC_3H_5)_2(CH_2CMe_3)_4$

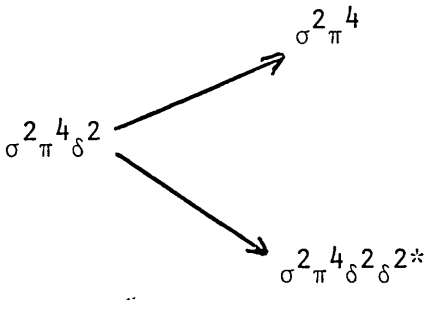
TABLE 7. SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR

$Os_2(\eta C_3H_5)_2(CH_2CMe_3)_4$

Os(2)-Os(1)	2.197(3)	C(1)-Os(1)	2.168(22)
C(2)-Os(1)	2.160(25)		
C(8)-Os(1)	2.199(25)	C(9)-Os(1)	2.107(21)
C(10)-Os(1)	2.214(23)		
C(3)-Os(2)	2.214(22)	C(4)-Os(2)	2.156(24)
C(5)-Os(2)	2.226(25)	C(6)-Os(2)	2.151(21)
C(7)-Os(2)	2.198(21)		
C(13)-C(1)	1.541(27)	C(14)-C(2)	1.601(30)
C(11)-C(3)	1.563(27)	C(12)-C(4)	1.566(29)
C(6)-C(5)	1.432(35)	C(7)-C(6)	1.433(33)
C(9)-C(8)	1.406(37)	C(10)-C(9)	1.457(33)
C(1)-Os(1)-Os(2)	97.0(5)	C(2)-Os(1)-Os(2)	103.0(6)
C(2)-Os(1)-C(1)	81.7(9)		
C(8)-Os(1)-Os(2)	122.6(8)	C(9)-Os(1)-Os(2)	105.5(6)
C(10)-Os(1)-Os(2)	114.6(6)		
C(3)-Os(2)-Os(1)	96.2(5)	C(4)-Os(2)-Os(1)	103.2(6)
C(4)-Os(2)-C(3)	82.8(8)		
C(5)-Os(2)-Os(1)	114.0(7)	C(6)-Os(2)-Os(1)	104.3(6)
C(7)-Os(2)-Os(1)	121.7(7)		
		C(30)-Os(3)-Os(3a)	103.8(13)
C(13)-C(1)-Os(1)	120.3(14)	C(14)-C(2)-Os(1)	129.6(17)
C(11)-C(3)-Os(2)	118.6(13)	C(12)-C(4)-Os(2)	129.7(16)

maximises any steric repulsions, and seems to indicate that steric influences are not the determining factor (although this probably does cause the observed trans disposition of the bulky neopentyl groups). This implies that electronic factors determine the conformation. However it is widely reported and even more widely accepted that in triple bonded species no electronic barrier to rotation exists, and it has been concluded that crystal packing forces ultimately determine the observed conformation (37). Whilst it may be true that they have an effect, I feel that the electronic contribution may have been underestimated.

Triple bonds can be considered as being derived from quadruple bonds in two ways, either by the loss of two bonding electrons, or by the gain of two anti-bonding electrons :



The former is exemplified by the Mo_2^{6+} and W_2^{6+} cores. In these cases there are no δ symmetry molecular orbitals and it is therefore reasonable to assume that there are no electronic constants on conformation, since no overlap of metal d_{xy} or $d_{x^2-y^2}$ is necessary to accomodate the available electrons. In these cases steric factors dominate and staggered conformations are observed.

However in the latter case there are fourelectrons in orbitals of δ symmetry. Generally it is accepted that these electrons (two bonding and two antibonding) cancel each other out. Whilst this is obviously true in terms of net attractive or repulsive force between the metal ions, they cannot be dismissed from the electronic configuration, and therefore neither can the orbitals containing them.

The presence of molecular orbitals with δ symmetry immediately imposes rotational constraints, any deviation from eclipsed stereochemistry causes a diminished overlap and thus raises the energy of the system. The limiting case of perfectly staggered geometry would preclude δ bond formation and the electrons would remain localised around the metal centres. Thus whilst the δ electrons do not exert any bonding effect, they may have a small but important effect on the preferred geometry, which is discernable in the absence of strong steric effects.

Examples to test this hypothesis are few, the Ru_2R_6 compounds (chapter 1) can only be isolated where R is a bulky alkyl group, steric factors dictate that a staggered conformation is observed. The other compound with a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration namely these with a Os_2^{6+} core, which are observed to have eclipsed geometries, contain bridging groups which may impose additional constraints on the conformation. The two useful examples are $Os_2(\eta C_3H_5)_2(CH_2CMe_3)_4$ and $Os_2Cl_8^{2-}$ (since they lack serious steric congestion) both of which have eclipsed geometry. As mentioned before crystal packing may be the dominant factor, studies are being conducted elsewhere (37) to determine the effect of such forces on rotational conformations.

The other salient features of the structure can be seen in Figures 5b and 5c. In figure 5b the ^{t}butyl groups of the neopentyl ligands have been omitted for clarity. Important bond angles and bond lengths are collected in Table 7, the numbering scheme is the same as that used in Figure 5c.

The constancy of the metal-carbon bond lengths (2·11 - 2·22 Å) indicate that the allyl moities are terminally bound η^3 ligands, chelating one metal centre as opposed to bridging the triple bond. All the ligands bend away from the metal-metal bond, presumably to minimise steric interactions. The angle between the normal to a plane containing all the allyl carbon atoms and the line described by the Os-Os bond is approximately 43^{o}.

The four carbon atoms of the neopentyl ligands also lie in a plane, even for the molecule which does not possess an inversion centre the maximum deviation of any carbon atom is 0.008 Å. The orthogonal displacement of the Os centres from this plane (0.801 and 0.809 Å) indicates how close this molecule is to being centrosymmetric.

The organometallic chemistry of osmium is somewhat limited in comparison to that of iron and ruthenium. There are only two other osmium allyl compounds (38), which have been fully characterised, this is the first osmium compound containing only hydrocarbon ligands to be structurally characterised.

TETRAKIS(CYCLOHEXYL)OSMIUM(IV)

The interaction of excess cyclohexyl Grignard reagent with $Os(O_2CMe)_4Cl_2$ in thf at low temperatures gives the title compound in approximately 25% yield. The compound is moderately air stable and soluble in hydrocarbons, especially aromatic hydrocarbons. It has been fully characterised by n.m.r, elemental analysis and single crystal x-ray diffraction.

This compound represents the first neutral, monomeric homoleptic alkyl of the platinum metals. Although a considerable number of such MR_4 compounds have been isolated for several of the early transition metals (Ti, Zr, Hf, V, Cr (39)) and also for Mo(40) and W(41) none were previously known for the platinum group metals.

Most of the afore mentioned compounds have been isolated at low temperatures, and only a few have been crystallographically characterised, namely $Ti(CH_2Ph)_4$ (42) $Zr(CH_2Ph)_4$(43), $Hf(CH_2Ph)_4$(42), V(mesityl)$_4$(44), $Cr(CH_2CMe_2Ph)_4$(45) and $Cr(CPh = CMe_2)_4$(46), (mesityl = 2,4,6 trimethylphenyl).

Recently a tetra-aryl analogue namely tetrakis(O-methylphenyl) Osmium(IV) has been prepared independently in these laboratories by the reduction of osmium tetroxide (47). A number of well defined tetra-aryl analogues are known, such as the tetra-mesityl compounds of Ti(48), Cr(49) and Mo(40) and these have received considerable attention due to their high thermal stability and chemical inertness in contrast to the well known intrinsic instability of phenyl via reductive elimination (50) or

ortho-hydrogen abstraction (51) pathways.

The thermal stability of the cyclohexyl compound is surprising, as it might have been expected to undergo facile β-hydride transfer, presumably as a result of which transition metal cyclohexyl compounds are relatively scarce (52) the closest analogue being tetrakis(cyclohexyl)titanium(IV) (53) which decomposes above -30°C.

The single crystal x-ray diffraction study reveals that the molecule has C_2 symmetry and that the coordination geometry is slightly flattened tetrahedral with C-Os-C angles of 105.3(2)° - 117.1(2)°. The Os-C bond lengths lie in the range 2.026(6)-2.030(3) Å. The cyclohexyl rings all lie approximately in chair conformations. No unusual interactions between the metal centre and the β-hydrogens on the cyclohexyl rings are discernable, these hydrogens were located in the x-ray diffraction study and are included in the molecular structure (figure 6). Selected bond angles and lengths are collected in Table 8.

This study reveals another novel feature of both this and the O-methoxyphenyl analogue in that they represent the first examples of tetrahedral Os(IV) species, previously only octahedral or distorted octahedral coordination geometry had been observed for this oxidation state.

This tetrahedral structure is in line with the observed diamagnetism of the compounds, consistent with an e^4 (low spin) electronic configuration.

The synthetic route used here is different to those employed in the

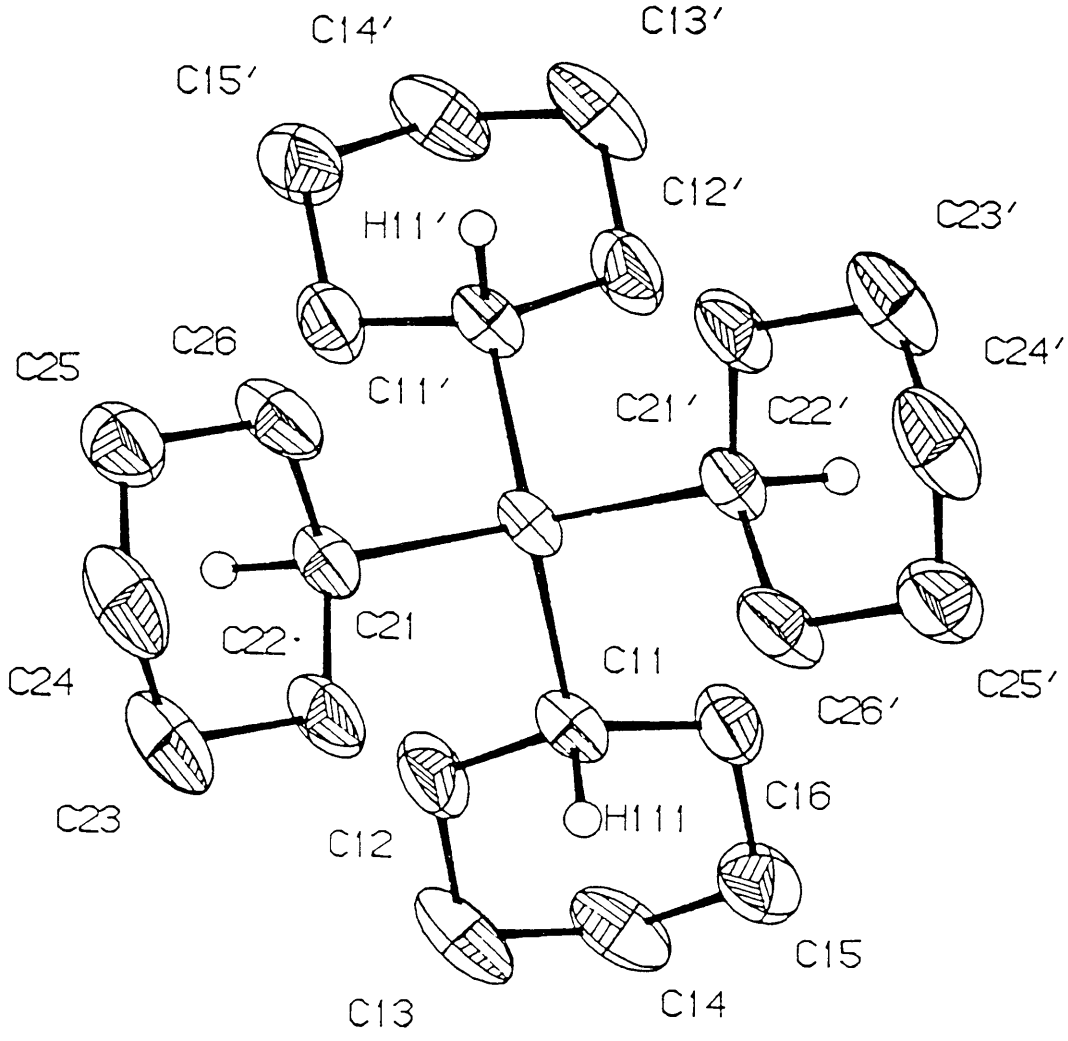


FIGURE 6: MOLECULAR STRUCTURE OF $Os(C_6H_{11})_4$

TABLE 8: SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR $Os(C_6H_{11})_4$

C(11)-Os(1)	2.031(8)	C(21)-Os(1)	2.026(8)
C(12)-C(11)	1.519(11)	C(16)-C(11)	1.532(11)
H(111)-C(11)	1.171(86)	C(13)-C(12)	1.529(12)
C(14)-C(13)	1.523(14)	C(15)-C(14)	1.510(13)
C(16)-C(15)	1.525(12)	C(22)-C(21)	1.519(12)
C(26)-C(21)	1.530(11)	H(211)-C(21)	1.189(79)
C(23)-C(22)	1.530(12)	C(24)-C(23)	1.503(14)
C(25)-C(24)	1.544(15)	C(26)-C(25)	1.527(12)

C(21)-Os(1)-C(11)	106.3(3)	C(12)-C(11)-Os(1)	113.8(5)
C(16)-C(11)-Os(1)	114.0(5)	C(16)-C(11)-C(12)	110.6(7)
H(111)-C(11)-Os(1)	100.1(42)	H(111)-C(11)-C(12)	108.5(40)
H(111)-C(11)-C(16)	109.2(40)	C(11)-Os(1)-C(11)	117.0(5)
C(13)-C(12)-C(11)	112.1(7)	C(14)-C(13)-C(12)	110.1(8)
C(15)-C(14)-C(13)	111.5(8)	C(16)-C(15)-C(14)	111.4(8)
C(15)-C(16)-C(11)	111.8(8)	C(22)-C(21)-Os(1)	114.7(5)
C(26)-C(21)-Os(1)	112.7(5)	C(26)-C(21)-C(22)	111.0(7)
H(211)-C(21)-Os(1)	107.9(39)	H(211)-C(21)-C(22)	107.4(37)
H(211)-C(21)-C(26)	102.3(38)	C(21)-Os(1)-C(21)	117.1(5)
C(23)-C(22)-C(21)	112.3(7)	C(24)-C(23)-C(22)	111.9(8)
C(25)-C(24)-C(23)	111.6(8)	C(26)-C(25)-C(24)	110.9(8)
C(25)-C(26)-C(21)	112.5(8)		

SELECTED NON BONDED DISTANCES (Å)

H(111)-Os(1)	2.516	C(12)-Os(1)	2.987
H(211)-Os(1)	2.645	C(16)-Os(1)	3.000

preparation of other tetra alkyls which have relied almost exclusively on metal halides or alkoxides. The mechanism of formation is still uncertain, it is conceivable that it proceeds via a disproportionation but it has not proved possible to isolate any other osmium containing species.

The interaction of $(C_6H_{11})MgBr$ with osmium tetroxide has been studied to see if this provides a more rational route to the tetra alkyls. This has been largely unsuccessful, the compound is formed (detected by ^1H n.m.r) but in very low yield, by the interaction of alkylating agent and osmium tetroxide in a mixture of diethyl ether and thf (3:1) at low temperature.

The analogous reaction with ruthenium acetate chloride gives an air sensitive, hydrocarbon soluble, orange-red crystalline compound. This has not yet been fully characterised, the i.r spectrum shows no bands attributable to acetate ligands, the ^1H n.m.r is complex, comprising of two multiplets centred at δ + 2.62 and δ + 1.58 ppm, the $^{13}C[^1H]$ spectrum consists of four sharp singlets at δ + 49.74, 33.50, 27.46 and 26.73 ppm. In the absence of analytical data it is not possible to distinguish the ruthenium(IV) monomer RuR_4 or the ruthenium (III) dimer Ru_2R_6 (R = cyclohexyl).

TABLE 5 N.M.R. DATA FOR THE OSMIUM ALKYLS

COMPOUND	CHEMICAL SHIFT, δ/ppm	
	^1H, J(Hz)	$^{13}C[^1H]$
$Os_2(O_2CMe)_2(CH_2CMe_3)_4$	3.92 s (8 $\underline{CH_2}$-CMe_3)	193.97 s $Me\underline{C}O_2$
	2.08 s (6 $\underline{Me}$-CO_2)	46.12 s $\underline{CH_2}$-CMe_3
	1.28s (36 $CH_2C\underline{Me_3}$)	44.09s CH_2-$\underline{C}Me_3$
		37.17s CH_2-$C\underline{Me_3}$
		28.10s $\underline{Me}CO_2$
$Os_2(O_2CMe)_2(CH_2SiMe_3)_4$	2.10 s (6 $\underline{Me}CO_2$)	179.8 s $Me\underline{C}O_2$
	1.42 s (8 $\underline{CH_2}SiMe_3$)	28.40 s $\underline{Me}CO_2$
	0.18 s (36 CH_2-$Si\underline{Me_3}$)	13.80 s $\underline{CH_2}SiMe_3$
		1.20 s $CH_2Si\underline{Me_3}$
$Os_2(\eta C_3H_5)_2(CH_2CMe_3)_4$	3.99 m (2, CH_2-$\underline{CH}$-CH_2)	102.00 s CH_2-$\underline{CH}$-CH_2
	3.40 s (8, $\underline{CH_2}$-CMe_3)	
	3.27 d (4, $\underline{CH_2}$-CH-$\underline{CH_2}$, $\underline{J}_{H-H}$ = 4	46.60 s $\underline{CH_2}$-CH-$\underline{CH_2}$
	1.50 d (4, $\underline{CH_2}$-CH-CH_2, $\underline{J}_{H-H}$ = 4	42.08 s $\underline{CH_2}$-CMe_3
	1.14 s (36, CH_2-$C\underline{Me_3}$)	34.84 s CH_2-$\underline{C}Me_3$
		24.37 s CH_2-$C\underline{Me_3}$

TABLE 6 ANALYTICAL DATA FOR THE OSMIUM ALKYLS

COMPOUND	COLOUR	m.p. θ/°C	FOUND (REQUIRED), %			
			C	H	O	Si
$Os_2(O_2CMe)_2(CH_2CMe_3)_4$	GREEN	184	34.9 (34.8)	a	8.2 (8.4)	
$Os_2(O_2CMe)_2(CH_2SiMe_3)_4$	BROWN	132	28.0 (28.3)	a	7.8 (7.6)	13.1 (13.2)
$Os_2(\eta^3C_3H_5)_2(CH_2CMe_3)_4$	ORANGE	113d		a		
$Os(C_6H_{11})_4$	RED	144	55.3 (55.2)	a		

a - No analysis possible for hydrogen in presence of osmium

CHAPTER 3

REACTIONS OF THE RUTHENIUM ALKYLS

CHAPTER 3. REACTIONS OF THE RUTHENIUM ALKYLS

INTRODUCTION

The reaction chemistry of dimolybdenum and ditungsten compounds containing triple metal-metal bonds has been extensively studied, much of this work has been reviewed (54).

These studies have concentrated exclusively on the amide or alkoxide compounds, $M_2(NR_2)_6$ or $M_2(OR)_6$. In contrast to this, the following chapter deals with the reaction chemistry of the triply bonded ruthenium per-alkyls described in Chapter 1. Generally it has been observed that the trimethylsilylmethyl compound exhibits greater reactivity than the neopentyl analogue, studies have concentrated more on the reactions of the former.

REACTION WITH PHOSPHINES

The hexa-alkyl $Ru_2(CH_2SiMe_3)_6$ reacts smoothly and rapidly with excess trimethylphosphine (PMe_3) in hexane at -30^oC to give (2,2,-Dimethyl-2-Silapropane-1,3-dyl)tetrakis(trimethylphosphine) ruthenium(II) [60% yield.]

$$Ru_2(CH_2SiMe_3)_6 + PMe_3 \longrightarrow (PMe_3)_4Ru\overline{-CH_2-Si(Me)_2-CH_2}$$

This compound has previously been obtained by the action of $(Me_3SiCH_2)_2Mg$ on ruthenium acetate chloride in the presence of PMe_3 (17a). The compound obtained in the present case has been identified by reference to the reported n.m.r. data.

The cleavage of metal-metal bonds by σ donors such as tertiary phosphines was known previously, one example is the cleavage of the ruthenium-ruthenium bond in $Ru_2(O_2CMe)_4Cl$ by triphenylphosphine (22). However simple addition products are more common (55) e.g

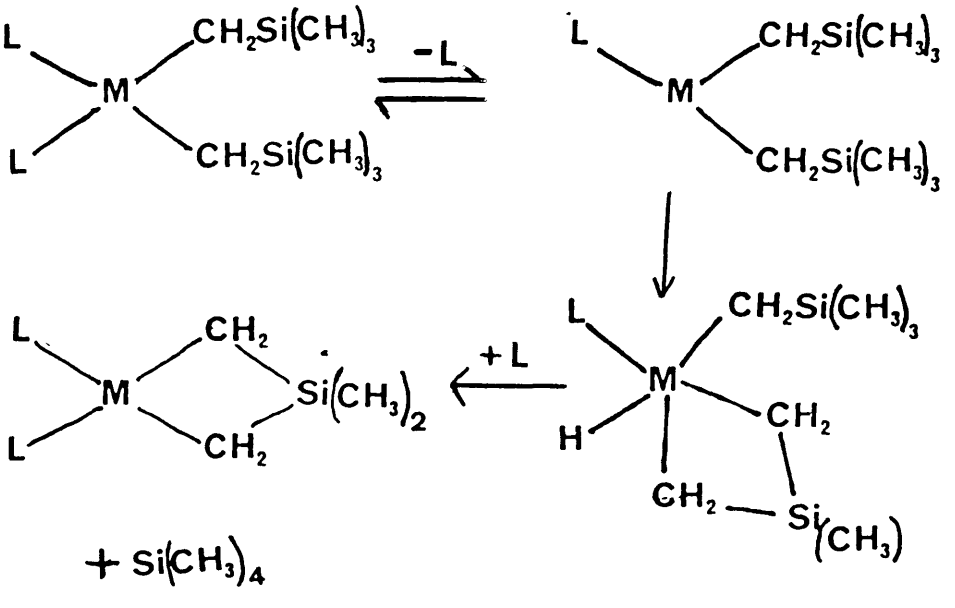
$$M_2(OR)_6 + 2L \longrightarrow M_2(OR)_6L_2$$

R = Me_3CCH_2, Me_3Si

L = NMe_3, $HNMe_2$, H_2NMe, PMe_2Ph.

But even in this type of reaction it has been postulated that mononuclear species may also be formed as minor products which are often not detected, $Re_2Cl_8^{2-}$ reacts with tertiary phosphines to give mainly the triple bonded $Re_2Cl_4(PR_3)_4$, but also some <u>trans</u> $ReCl_4(PR_3)_2$. (56).

Metallocycles such as those formed in the present reaction have been extensively studied (57) since the recognition of their importance in various catalytic processes such as alkene metathesis. The cyclometallation of the trimethylsilylmethyl group has been observed previously (58), the most widely proposed mechanism is via γ-hydride elimination.



The phosphine induced reductive elimination of alkane (final step) has been reported (59). In the present case this mechanism cannot fully explain the formation of the final product. The important point is that the above mechanism does not produce any net change in oxidation state of the metal, since it comprises of an oxidative addition followed by a reductive elimination, during the formation of the metallocycle from the hexa alkyl reduction has occured at both metal centres.

Another reason why this cannot be the only process occuring is the presence of an odd number of alkyl groups attached to each metal centre. The formation of a metallocycle and expulsion of one molecule of tetramethylsilane would leave a metallocycle plus one alkyl group attached to each ruthenium, this lone alkyl group could not be removed by another mononuclear cyclization. Several alternatives may be envisaged, including reductive elimination of $(Me)_3Si-(CH_2)_2-Si-(Me)_3$ from separate metal centres, alkyl migration (promoted by phosphine coordination) followed by reductive elimination of the above alkane from a single metal centre, or by some other stepwise elimination process involving both metal centres via an alkyl or alkylidene bridge. The yield being greater than 50% precludes disproportionation mechanism. The above all assumes that cyclisation is the first step, but there is no evidence to support this and it may be preceded by cleavage. Another alternative is that the reaction may proceed wholly or in part by radical processes. One other point worthy of note is that excess phosphine is required, stoichiometric ammounts give the same product but in greatly reduced yield.

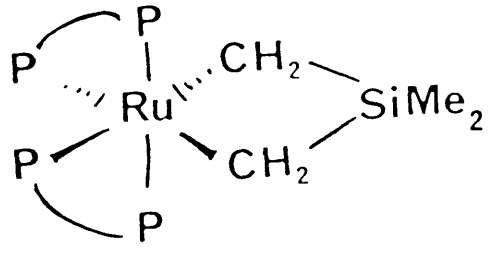
Overall the evidence available is not sufficient to elucidate the mechanism, no attempt has been made to identify the organic by-products of the reaction. However the result is interesting both in its own right as a phosphine induced cleavage of a metal-metal triple bond and also in view of the previously cited work of Andersen et al(17a). These authors proposed a mechanism similar to that shown above, going via initial formation of a dialkyl species, no explanation was offered of how the reduction of the ruthenium centres occured on going from the acetate chloride (net oxidation state 2.5) to the divalent alkyl. The results now available seem to suggest that this could occur as follows, initially $(Me)_3Si-CH_2MgCl$ merely acts as a soluble reducing agent in thf (see chapter 1), the produced tetraacetate is cleaved by phosphine (observed to be a facile reaction(60)) and the two remaining acetate groups per ruthenium are then removed by the action of more Grignard reagent. Additional evidence is that the reaction is much slower in diethyl ether, in this solvent reduction by the Grignard does not occur, here presumably cleavage by phosphines is an important step (no mention is made of a green colour in the original paper, suggesting that the hexa alkyl is not formed).

Thus it is tempting to speculate that whilst both the reaction of Andersen (17a) and that between the ruthenium alkyl and PMe_3 described here, use exactly the same reagents and ultimately produce the same product, the intermediates are different, the course determined at least in part by the choice of solvent.

The reaction between the ruthenium hexa-alkyl and dmpe proceeds under slightly more forcing conditions than those necessary for

the analogous reaction with PMe_3.

Following the first recrystallization from hexamethyldisiloxane, the major product (in the form of yellow needles) is contaminated with a red oil. The $^{31}P[^1H]$ n.m.r spectrum indicates the presence of free phosphine, and also shows a sharp singlet at δ + 37 ppm, these can be removed by repeated recrystallizations. The major product shows two triplets in the $^{31}P[^1H]$ n.m.r spectrum, one centred at δ + 13 ppm (J_{p-p} = 14 Hz) and the other at δ + 21 ppm (J_{p-p} = 15 Hz). Although good elemental analytical results could not be obtained, the spectroscopic evidence suggests that this compound has a similar structure to that of the PMe_3 compound, containing a metallocyclic ring, and two dmpe ligands giving a propeller structure.



REACTION WITH DIOXYGEN

The ruthenium alkyls are very sensitive to air and moisture, the trimethylsilylmethyl compound is pyrophoric in the solid state and decomposes rapidly in solution. If the contact with air is minimal a transient red colour is discernable prior to complete decomposition. Efforts were made to characterise this red compound.

Very few attempts have been made or at least reported (61) to characterise the products of reactions between "air sensitive" organometallic compounds and air, because of this and also in the light of reports that the decomposition of sensitive organometallic compounds on oxidising or acidic supports (such as alumina) give highly active catalysts (62), the identity of the red species is of interest.

The compound can be prepared in moderate yield by the action of dry oxygen (one equivalent per dimer) added via syringe to a hexane solution held at -80°C. The red crystalline air sensitive compound is very soluble in aromatic and alphatic hydrocarbons. Elemental analyses indicated the stoichiometry $RuOR_3$, molecular weight measurements (cryoscopically in benzene) revealed a dimeric structure, and the i.r. spectrum in addition to bands attributable to the alkyl groups showed a strong band at 908 cm^{-1}, presumably due to a ruthenium-oxygen double bond. The ^1H n.m.r spectrum was largely uninformative consisting of two singlets, similar in position to those of the present alkyl but severely broadened, the $^{13}C[^1H]$ spectrum shows two sharp singlets, shifted downfield with respect to the pure alkyl, possibly reflecting the deshielding nature of the oxo ligands (63).

In order to ascertain in more detail the nature of oxygen coodination a single crystal x-ray diffraction study was undertaken. The structure is shown in Figure 7, selected bond lengths and alkyls are collected in Table 9.

From this it can be seen that molecular oxygen has been cleaved and one oxo ligand is attached to each ruthenium centre. The molecule is centrosymmetric and the coordination geometry around ruthenium can best be described as distorted trigonalbipyramidal, with C1, C2 and O1 forming the equatorial plane (e.g the bond angle C2-Ru1-C3 = 119.4°) and C1 and the other ruthenium centre Ru2 occupying the axial positions. The slight deviation from linearity of the C1-Ru1-Ru2 axis is presumably due to the weak interaction of the oxo ligand O1B with Ru1 vide infra. This compound is thus formally a Ru^{5+}- Ru^{5+} dimer, a rare oxidation state for ruthenium, the only well characterised examples being the pentafluoride (64) and a number of ruthenates (65). The M_2^{10+} core is not known for other platinum metals, but does have an analogue in molybdenum chemistry (66), a similar comparison between the compounds of molybdenum and ruthenium was made in Chapter 1 in the discussion of the Ru_2R_6 species. The Ru-Ru bond length of 2.737 Å falls into the range typical of Ru-Ru single bonds, for example that in the tetrameric ruthenium nitrosyl complex $[Ru_4(NO)_4Cl_4(PPH_2)_4]$ is 2.787 Å (67). The coordination of the oxo ligands can best be described as a metal-oxygen double bond, and a weak donation from this doubly bonded species to the other ruthenium centre in the dimeric unit. The shorter bond length of 1.714 Å is indicative of a metal-oxygen double bond, similar to that seen in other high valent ruthenium oxo compounds (65). The longer Ru-O distance of 2.231 Å, lies outside the region usually associated with Ru-O single bonds ($\sim$ 2.0 Å) as seen in the carboxylates, and resembles more the weak interaction observed between ruthenium and oxygen donors such as thf or acetone ($\sim$ 2.3 Å) (see Chapter 4).

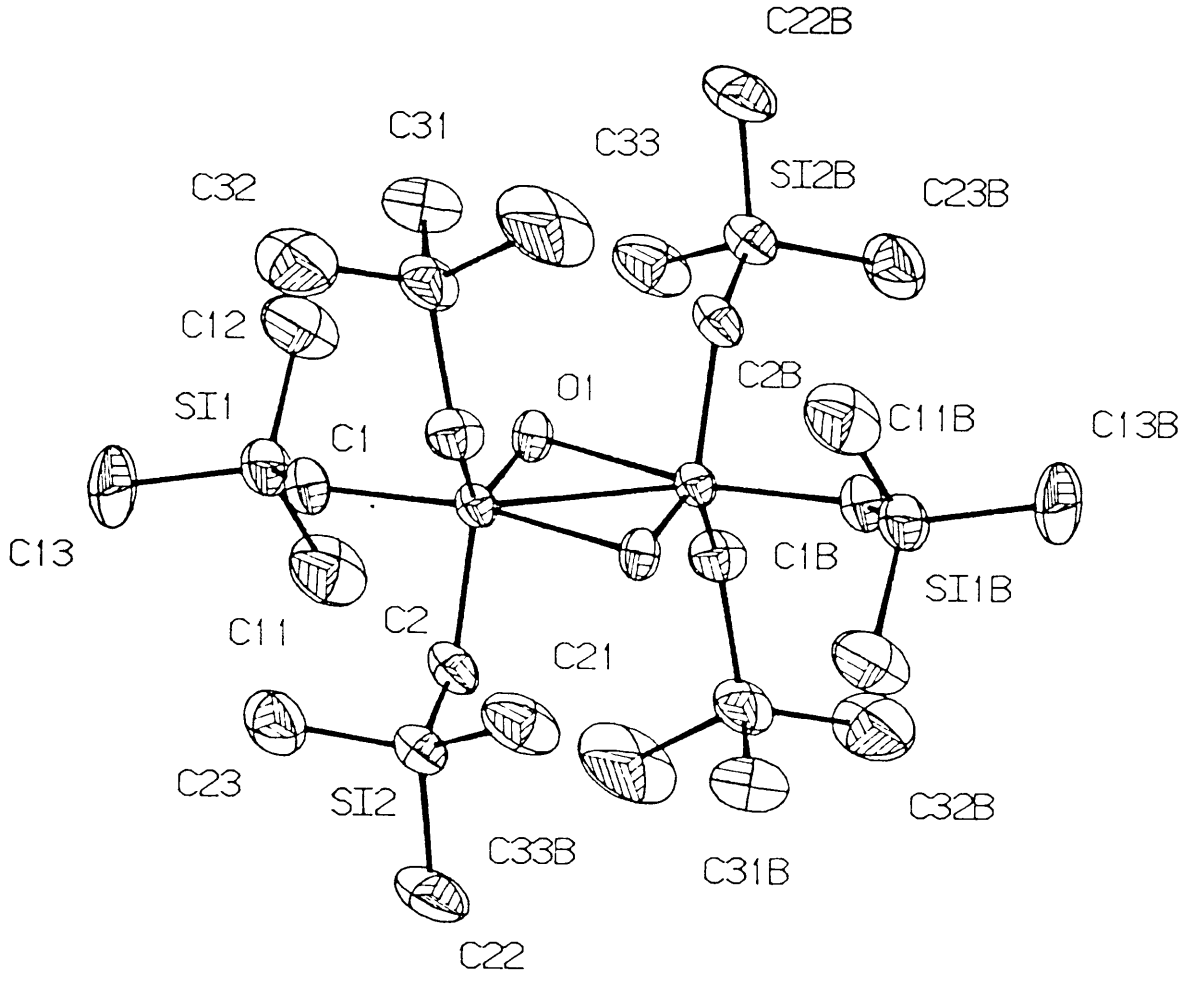


FIGURE 7. MOLECULAR STRUCTURE OF $Ru_2O_2(CH_2SiMe_3)_6$.

TABLE 9: SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR

$Ru_2O_2(CH_2SiMe_3)_6$

O(1)-Ru(1)	1.733(6)	C(1)-Ru(1)	2.071(8)
C(2)-Ru(1)	2.031(8)	C(3)-Ru(1)	2.027(8)
Ru(1)-Ru(1a)	2.738(4)	O(1)-Ru(1a)	2.208(6)
C(1)-Si(1)	1.869(8)	C(11)-Si(1)	1.871(9)
C(12)-Si(1)	1.862(9)	C(13)-Si(1)	1.876(9)
C(2)-Si(2)	1.876(8)	C(21)-Si(2)	1.860(9)
C(22)-Si(2)	1.860(8)	C(23)-Si(2)	1.865(8)
C(3)-Si(3)	1.880(8)	C(31)-Si(3)	1.852(9)
C(32)-Si(3)	1.863(9)	C(33)-Si(3)	1.858(10)
H(11)-C(1)	0.855(39)	H(12)-C(1)	1.047(38)
H(21)-C(2)	0.897(32)	H(22)-C(2)	1.053(31)
H(31)-C(3)	0.730(32)	H(32)-C(3)	0.865(37)
C(1)-Ru(1)-O(1)	101.8(3)	C(2)-Ru(1)-O(1)	118.5(3)
C(2)-Ru(1)-C(1)	88.3(3)	C(3)-Ru(1)-O(1)	120.7(3)
C(3)-Ru(1)-C(1)	89.2(4)	C(3)-Ru(1)-C(2)	119.9(4)
C(11)-Si(1)-C(1)	112.6(4)	C(12)-Si(1)-C(1)	112.2(4)
C(12)-Si(1)-C(11)	107.8(5)	C(13)-Si(1)-C(1)	106.1(5)
C(13)-Si(1)-C(11)	109.5(5)	C(13)-Si(1)-C(12)	108.5(5)
C(21)-Si(2)-C(2)	112.6(4)	C(22)-Si(2)-C(2)	105.2(4)
C(22)-Si(2)-C(21)	108.9(4)	C(23)-Si(2)-C(2)	111.4(4)
C(23)-Si(2)-C(21)	109.5(5)	C(23)-Si(2)-C(22)	109.1(4)
C(31)-Si(3)-C(3)	115.0(4)	C(32)-Si(3)-C(3)	108.8(4)
C(32)-Si(3)-C(31)	107.4(5)	C(33)-Si(3)-C(3)	106.8(4)
C(33)-Si(3)-C(31)	108.1(5)	C(33)-Si(3)-C(32)	110.7(6)
Si(1)-C(1)-Ru(1)	118.5(4)	H(11)-C(1)-Ru(1)	104.4(20)
H(11)-C(1)-Si(1)	107.6(27)	H(12)-C(1)-Ru(1)	114.3(20)
H(12)-C(1)-Si(1)	106.2(23)	H(12)-C(1)-H(11)	104.8(35)
Si(2)-C(2)-Ru(1)	118.9(4)	H(21)-C(2)-Ru(1)	109.1(23)
H(21)-C(2)-Si(2)	111.2(24)	H(22)-C(2)-Ru(1)	97.8(24)
H(22)-C(2)-Si(2)	97.9(26)	H(22)-C(2)-H(21)	121.7(32)
Si(3)-C(3)-Ru(1)	122.5(4)	H(31)-C(3)-Ru(1)	106.6(32)

Metal oxides are being increasingly used in industry and academia to effect organic transformations both as stoichiometric reagents and as catalysts. Important processes catalysed by metal oxides include olefin metathesis, oxidation and expodation. Despite their increasing use relatively little is known about their mode of action. Elucidation is made more difficult when (as is true of many of the afore mentioned cases) the metal oxides act as heterogeneous catalysts. Because of this, great interest and effort is being chanelled into synthesizing stable, tractable transition metal oxo compounds, whose interaction with organic molecules can be studied in depth using conventional spectroscopic techniques such as n.m.r.

In recent years interest in transition metal oxo species has also been stimulated by the large body of evidence that has been presented implicating metal oxo species as the active oxidants in reactions mediated by the cytochrome P450 containing monooxygenases which catalyse a variety of alkane oxidations (68).

Oxide compounds are known for all of the elements except the lighter noble gases, but those containing terminal multiply bonded oxo ligands are limited. Amongst the transition elements those of metals in groups 5-7 and the iron triad have been reviewed(69), in addition to this extensive work on organometallic rhenium oxo compounds has been reported (70). Titanium compounds containing a terminal oxo ligand and a nitrogen bonded macrocycle are known (71).

Oxidation sources other than molecular oxygen are generally used in the preparation of these compounds, more typically employed

are peroxides, periodates, hypochlorites, iodosylbenzene (C_6H_5IO), tertiary amine oxides, or aromatic nitro and nitroso compounds. For example the reaction of the molybdenum dimer $Cp_3Mo_2(CO)_4$ with $PhNO_2$ or PhNO gives the same product which contains both bridging and terminal oxo ligands (72). Similarly the ruthenium oxo-alkyl can be prepared in good yields (>70%) by the reaction of Ru_2R_6 with nitrosobenzene in toluene at -80°C. Even at this low temperature the reaction is instantaneous. The product can be crystallized directly from the reaction solution, the by-product azobenzene can also be isolated.

The synthesis of metal oxo compounds using molecular oxygen is much less common. Examples include the reaction of the postulated (but unisolated) "ReR_4" species with air or oxygen to give the known $ReOR_4$ (73). It was later shown(61) that $ReOMe_4$ could be further oxidised by air to give ReO_3Me. More recently it has been reported (63) that the photolysis of $(\mu^5C_5Me_5)Re(CO)_3$ in the presence of oxygen gives $(\mu^5C_5Me_5)Re\ O_3$, containing three terminal oxo ligands. Reaction of this compound with a reducing agent (triphenylphosphine) leads to the formation of a dimer containing both terminal and bridging oxo ligands (74).

Various ruthenium (VI) oxo compounds are known including those containing nitrogen donor ligands such as ammines (75) or macrocycles (76). However this compound is the first stable Ru(V) oxo compound, recently it has been reported that the reduction of a ruthenium(VI) dioxo compound (76a) with triphenylphosphine gives a Ru(IV) oxo species from which Ru(V) species can be generated electrochemically in solution (77).

The corresponding neopentyl compound $Ru_2O_2(CH_2CMe_3)_6$ cannot be prepared by the direct action of oxygen on the hexa-alkyl, but can be made in moderate yield using nitrobenzene. It is a dark orange-red crystalline compound, whose spectroscopic properties are similar to the trimethylsilylmethyl compound. The i.r. spectrum shows a band at 926 cm^{-1} and the $^{13}C['H]$ resonances are shifted downfield with respect to the parent alkyl.

Reactions between the alkyls and other substrates which can potentially oxidatively add were largely unsuccessful. Reaction with chlorine gas or gaseous HCl lead to the rapid formation of $RuCl_3$ even at low temperature, those with bromine and iodine gave intractable products. The reaction with iodosylbenzene in toluene gave a red colour at low temperature but decomposed above -15^oC.

The oxo alkyls are useful starting materials in their own right and their reaction chemistry will be discussed later. The compounds also have some catalytic significance potentially both as model compounds and active catalysts in their own right. The only type of catalytic behaviour that has been studied to date is that towards alkene epoxidation, before giving experimental details it may be informative to outline the general principles and existing processes.

Although the direct interaction of molecular oxygen with alkenes to give carbonyls and epoxides is thermodynamically favourable, it is prevented by kinetic reasons being both symmetry and spin forbidden (since O_2 has a triplet ground state).

Oxidation can occur via non concerted radical chain reactions,

often involving attack at the reactive allylic C-H bond, such processes give complex mixtures of products and are thus of little use.

Consequently much work has been aimed at producing metal catalysts which can control this oxidation to give the required products, proceeding via non-radical ionic pathways.

To this end much effort has been devoted to the homogeneous activation of molecular oxygen by metal complexes. A variety of metal dioxygen compounds have been synthesized and reactions with alkenes studied (78) . With one exception (79) most attempts to oxidise hydrocarbons using dioxygen complexes have been unsuccessful, several reasons have been postulated for this failure (80),

This research effort has produced several active catalysts, these can be broadly subdivided according to their mode of action. The first involve alkylperoxymetal intermediates, the second oxo-metal species.

Although the first type are more widely used in industry little will be said of them here. A prime example is the epoxidation of propene by alkylhydroperoxides in the presence of molybdenum catalysts

$$CH_3\text{-}CH = CH_2 + R\text{-}O\text{-}OH \xrightarrow{Mo} CH_3\text{-}CH\overset{O}{\frown}CH_2 + ROH$$

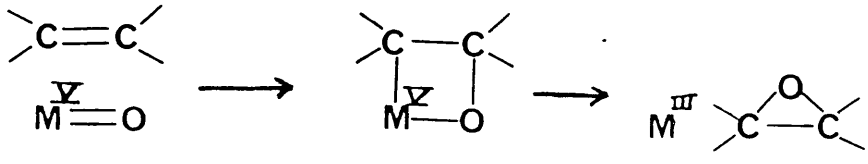
This illustrates an important feature of this route namely stoichiometric co-product formation, for each mole of epoxide one

mole of alcohol is produced. The economic viability of the process depends on the commercial value of the alcohol (81) . This is a major barrier to the efficient air epoxidation of alkenes, only one oxygen atom from the original dioxygen molecule is transferred to the organic product, this is true of the heterogeneous oxidation of ethylene

$$7/6\ C_2H_4 + O_2 \xrightarrow{Ag} C_2H_4O + 1/3\ CO_2 + 1/3\ H_2O$$

To overcome this, the symmetrical cleavage of dioxygen such as that produced by the ruthenium alkyl is desirable, where both oxygen atoms are available for oxidative reactions. Symmetrical cleavage of O_2 and subsequent oxygen atom transfer to organic molecules has previously been achieved using metal nitrosyls (82) .

The second type of catalysts i.e. those involving metal-oxo species is more relevant to present studies. This class includes OsO_4 and SeO_2. It has been postulated that oxo species act as carbenic reagents. The mechanism for both alkene epoxidation and oxidative cleavage is widely thought to proceed via a four membered metallocycle



Such a mechanism has been proposed for alkene epoxidation by $Cr_2O_2Cl_2$ (83) and is comparable to that suggested for olefin metathesis (84) .

Having given some background to the industrial oxidation of

alkenes, something will now be said with reference to a compound prepared here. The interaction of the ruthenium(v) oxo-alkyl (described above) with propene has been studied by 'H n.m.r and solution i.r. spectroscopy. The evidence suggests that the products are propene oxide and the hexa-alkyl Ru_2R_6.

N.M.R STUDIES

As mentioned above it has proved possible to study the reaction using 'H n.m.r. A spectrum of propene can easily be obtained by bubbling it through a deuterated solvent contained in an n.m.r tube. The spectrum consists of a doublet at δ + 4.95 and a broad multiplet centred at δ + 5.65. The spectrum of the corresponding epoxide contains a doublet at δ + 1.3, a multiplet at δ + 3 and two symmetrical multiplets centred at δ + 2.5. The spectrum of the oxo alkyl is of little diagnostic use being broad and ill resolved. The signal due to the methylene ($-CH_2-$) protons in the produced Ru_2R_6 species occurs at δ + 1.51 and is therefore almost coincident with a peak due to the alkene, but the intensity and multiplicity of these signals allows a distinction to be made. The methyl protons of the Ru_2R_6 species are very apparent, coming at much higher field (δ + 0.21). Usually during the course of the reaction it proved possible to discern the removal of the multiplets at δ + 5.65 and δ + 4.95, and a doublet shift upfield from δ + 1.45 to δ + 1.30, plus the sharpening of the singlet at δ + 0.21. Using these observations as guidelines, the reaction was studied in three ways.

Method (i)

To a solution of propene in C_6D_6 contained in an n.m.r. tube, previously slowly cooled to approximately -10°C was added a solution of $[RuO(CH_2SiMe_3)_3]_2$ also in C_6D_6, the very low temperature ensured that the oxo alkyl solution froze almost immediately thereby limiting reaction. (It should be stressed that if the benzene solution of the alkene is cooled too rapidly or tc much below -10°C, alkene concentration decreases dramatically).

The frozen reaction mixture was then transferred to the probe of the spectrometer (also previously cooled to -10°C), and allowed to warm slowly to +6°C (just above the melting point of C_6D_6) and held at this temperature whilst a spectrum was recorded. At temperatures this close to the melting point resolution was poor, but it appeared that no reaction had occured. The temperature was allowed to rise to +10°C over the course of about five minutes, when a new spectrum was recorded it showed that reaction had begun, with both starting material and product visible, but no intermediate species. After holding the sample at this temperature for five minutes another spectrum was recorded, which showed much smaller peaks due to the alkene. Soon after this time decomposition was apparent, within ten minutes a black precipitate was discernable this was accompanied by a decrease in the intensity of peaks due to a propylene oxide. The above is a description of an ideal run, several attempts were necessary to optimise conditions, equimolar quantities or even a slight excess of metal species over alkene was found to enhance resolution.

Method (ii)

In an attempt to trap intermediate species, the reaction was repeated in deuterotoluene C_7D_8, so that lower temperatures could be used, the lowest feasible temperature proved to be $-70^{o}C$. No reaction was observed at this temperature, and so the mixture was allowed to warm slowly, reaction occured rapidly around $-30^{o}C$, again without observable intermediates. Despite repeated attempts to control the rate of reaction by holding the temperature constant and taking spectra as a function of time, or by taking spectra every few degrees no intermediate species could be detected. Another disadvantage of this method is that signals due to protiotoluene species add to the complexity of the spectrum.

Method (iii)

When the reaction was conducted on a larger scale it proved possible to isolate propylene oxide. To a solution of alkene in hexane held at $-40^{o}C$ was added a cooled solution of the oxo alkyl also in hexane, the reaction was allowed to warm to $-30^{o}C$ and stirred for five minutes during this time the solution became dichroic red-green in colour. (At this stage aliquots were taken for i.r. studies, see below). To the reaction solution was added a mixture of thf/water to destroy the alkyl and thus quench the reaction, rapid decomposition was evident. The black reaction mixture was then distilled, the fraction boiling between $35-36^{o}C$ was collected. To this was added C_6D_6 and the ^1H n.m.r spectrum recorded, which showed peaks characteristic of propylene oxide.

INFRA-RED STUDIES

Solution i.r. spectra were obtained using matched KBr solution cells. The principle bands monitored were the propene carbon-carbon double bond stretch at 1670 cm^{-1}, which disappears during the reaction, and strong propylene oxide bands at 1260 and 950 cm^{-1} which appear in the final spectrum. The metal oxo stretch was obscured by bands due to the organic substrates. Many other strong bands were either common to both alkene and epoxide or partially obscured by residual solvent peaks.

Aliquots were taken from a reaction mixture prepared as outlined in section (iii) of the n.m.r studies above. Decomposition of the samples was evident when allowed to warm to room temperature, to prevent solids from being introduced into the i.r. cells, the aliquot was first transferred to another flask at room temperature and then filtered into the cells.

As it stands the oxidation of alkenes is stoichiometric, to complete the cycle (figure 8) and make the process catalytic a source of oxygen is needed.

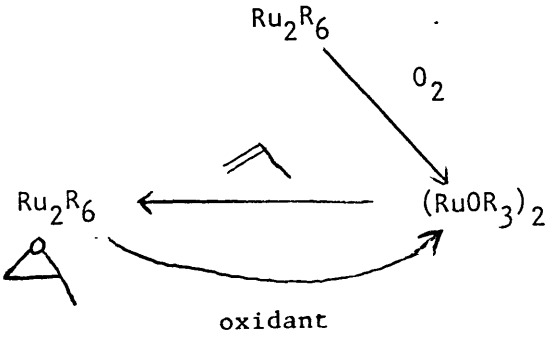


Figure 8 , Interaction of Ruthenium Oxo Alkyl with Propene.

The sensitivity of both the alkyl and the oxo alkyl precludes the use of air or molecular oxygen, decomposition also results from the use of peroxides or any of the other classical oxidants mentioned in the introduction. One candidate is nitrosobenzene (PhNO) which reacts smoothly and rapidly with Ru_2R_6 species to give the oxo alkyls, but this takes the process back into the area of stoichiometric co-product formation (in this case azobenzene). Another possible alternative is iodosylbenzene prolonged exposure of the trimethylsilylmethyl alkyl to this compound, whilst apparently forming the oxo-alkyl eventually leads to decomposition, the reaction of the analogous neopentyl compound has not been attempted, but the much reduced general reactivity of this compound is encouraging, and it may survive prolonged contact with PhIO, however the ability of this compound to epoxidise alkenes has not yet been studied, and again the process would result in co-product formation.

The high reactivity of both the oxo-alkyl and the parent alkyl present serious problems. The air sensitivity not only prohibits the use of oxygen or air as oxidising agents, but also presents serious handling problems when working on anything above centigram scales. The other possibly more serious manifestation of this reactivity is that the alkyl species appear to react to some extent with epoxides, prolonged reaction times cause the ammount of epoxide present to decrease dramatically. Another disadvantage common to all platinum metal "catalysts" is the high cost which often proves prohibitive, in the present case the active species is produced only after several succesive reactions:

$$Ru \longrightarrow RuCl_3 \longrightarrow Ru_2(O_2CMe)_4Cl \longrightarrow Ru_2R_6 \longrightarrow (RuOR_3)_2$$

after the first stage, the yields are all poor and this means high initial financial outlay to produce a "catalyst" known to have a short lifetime. The solution would be to produce a similar species with the same activity from a much cheaper metal source. One obvious candidate is molybdenum, given the current use of some of its compounds as epoxidation catalysts, and the existence of molybdenum analogues of the ruthenium alkyls Mo_2R_6 (24). Preliminary studies have failed to obtain oxo-alkyl species from the reaction of these alkyls with molecular oxygen, the reaction between them and nitrobenzene or iodosylbenzene has not yet been studied.

Although the afore mentioned disadvantages probably prevent the ruthenium oxo-alkyls from being useful catalysts in their own right, they may still prove interesting as model compounds, because as mentioned in the introduction relatively little is known about the interaction of metal oxo species with organic molecules. For the present studies propene was selected because of the industrial importance of its oxidation, however this system has two main disadvantages. First the large rate of reaction prevented the detection of intermediates, and secondly being a gas at room temperature, propene proved difficult to study. It may thus prove more rewarding to study the reaction using other alkenes such as styrene.

To date studies have been confined to alkene epoxidation but as mentioned in the introduction, metal-oxo species have been used in many other processes, the work could be extended to investigate these. Two notable examples are alkene metathesis and alcohol oxidation, the latter is especially relevant since Ru(VI) oxo

species are known to effect such transformations and the previously cited electrochemically generated Ru(V) oxo species has been shown to be active for the oxidation of benzyl alcohol (85).

REACTIONS OF THE OXO-ALKYLS

As mentioned before the novelty of the dimeric Ru(V) oxo alkyls makes them attractive starting materials, three reactions are outlined below.

IMIDO COMPOUNDS

i) Hexakis(trimethylsilylmethyl)bis(n-phenylimido)diruthenium(V)

The oxo alkyl reacts rapidly with excess phenyl-isocyanate in hexane at $-30^{o}C$ to give the phenylimido derivative $Ru_2(N\text{-}C_6H_5)_2(CH_2SiMe_3)_6$ in low yields. This air sensitive compound is insoluble in hexane and chlorinated hydrocarbons, only slightly soluble in benzene but more so in toluene. This insolubility hampers n.m.r studies, the only solvent that can be used sucessfully is toluene (the compound decomposes in acetone or thf) and this obscures the aromatic region especially in the $^{13}C['H]$ spectrum. The 'H spectrum shows two broad singlets at δ + 0.38 and δ + 1.62 ppm for the alkyl ligand protons and two multiplets in the aromatic region.

The i.r. spectrum contains a strong band at 1610 cm^{-1} again characteristic of an aromatic group, but it is difficult to assign with certainty the position of the Ru-N stretch. However there is a strong band at 1132 cm^{-1}, which is not present in the spectrum of the oxo-alkyl, this falls in the correct region for

such species (29). Elemental analytical data are in good accord with the formulation given. The interaction of metal-oxo species with alkyl or aryl isocyanates to give imido species has been reported previously (86).

ii) Hexakis(trimethylsilylmethyl)bis(N-trimethylsilylimido) diruthenium(v)

The oxo alkyl will react in hexane at room temperature with the phosphinimine $Me_3P = NSiMe_3$ over the course of a day to give the title compound in low yield, the other product, detected by $^{31}P['H]$ n.m.r spectroscopy is trimethylphosphine oxide ($O=PMe_3$).

This orange, air sensitive crystalline compound is more soluble than the phenylimido analogue, allowing the $^{13}C['H]$ spectrum to be recorded, in addition to signals at due to the alkyl ligand, a new singlet at δ - 4.8 ppm has appeard. Once again it is difficult to assign the Ru-N band unequivocally in the i.r. spectrum but there is a sharp peak at 1160 cm^{-1}. As for the phenylimido analogue the method of preparation is not new, the reaction of phosphinimines with metal oxo species has been widely used to produce imido complexes (87) .

REACTION WITH TRIMETHYLALUMINIUM

The oxo alkyl reacts rapidly in hexane at $-30^{o}C$ with a solution of trimethylaluminium (also in hexane). An immediate colour change from red to pale yellow is discernable and is accompanied by formation of a white precipitate (presumably alumina). Recrystallization of the product from hexane gives a white

crystalline, paramagnetic solid, which is very air and moisture sensitive, elemental analysis indicates the presence of only carbon and hydrogen, but no more is known at present concerning its identity.

MISCELLANEOUS REACTIONS

It has not yet proved possible to isolate homoleptic alkoxide or amide compounds pure, several synthetic routes have been tried including the interaction of lithium and magnesium amides or alkoxides with ruthenium acetate chloride and the reaction of alcohols and secondary and primary amines with the hexa-alkyl species.

Little reaction is observed when lithium or magnesium amides are used, perhaps reflecting their inability to promote a disproportionation, only faint red colours are detectable when the reaction residues are extracted with toluene. Similar reactions using LiO^tBu were even less successful, a black insoluble precipitate formed rapidly when reactions reached room temperature.

It was hoped that the direct interaction of alcohols or amines with the alkyl compound would liberate alkane and give alkoxide or amide species. However no reaction is discernable between Ru_2R_6 and dimethylamine and the action of methanol, ethanol or propanol causes rapid decomposition. Addition of phenol to a solution of the alkyl gives a rapid colour change to deep red. Removal of volatile materials, followed by removal of phenol (by vacuum sublimination) leaves an air sensitive brown powder, soluble in aromatic hydrocarbons and acetonitrile. In addition to those due to aromatic protons, the ^1H n.m.r contains signals at higher field, indicating the presence of groups other than phenoxide. It is not clear if this powder is one compound or a mixture containing other organic or metallic species, attempts to purify this powder further have so far been unsuccessful. Addition of a solution of ^{t}butanol

to the hexa-alkyl ultimately gives a red-purple oil, which is difficult to separate from excess free alcohol, once again analytical and spectroscopic data indicate the presence of more than one species.

Neither of the hexa alkyls react with diazomethane, or with ethylene even at elevated temperatures or pressures or photolytically. As mentioned before reactions between the alkyls and species that can potentially oxidatively add (such as halogens) have failed to give isolable products, whilst that with HX (X = halogen) gives the trihalide, RuX_3.

It has not proved possible to isolate any hydride species formed from the alkyls. The action of hydrogen leads to rapid decomposition, giving alkane and metallic ruthenium, other attempts using sodium hydride and/or hydrogen in the presence of crown ethers have also been unsuccessful.

The thermal rearrangement of the trimethylsilylmethyl compound has been studied by n.m.r. When a sample of this compound in C_7D_8 is held at 80°C for six hours, a colour change from green to red is discernable. In addition to a large sharp singlet due to tetramethylsilane (TMS), the ^1H n.m.r spectrum consists of two sharp singlets at δ + 0.18 ppm and a broad singlet at δ - 1.45 ppm. The $^{13}C[^1H]$ n.m.r spectrum also shows the presence of TMS, plus sharp singlets at δ + 253.8, +15.6, + 0.3, - 10.8 ppm. The low field line is indicative of a carbon centre in an alkylidene or alkylidyne functionality, which could conceivably arise from an α-hydride transfer from the trimethylsilylmethyl group in the hexa-alkyl, followed by reductive elimination of the alkane, TMS

(which is observed). Consistent analytical data for this red air sensitive solid has not yet been obtained. One interesting point is that this thermal reaction does no occur in solvents other than toluene, no colour change occurs when a solution of the alkyl in high boiling petroleum ether (b.p 100-120°C) is held at 80°C for 24 hours, prolonged heating or higher temperatures both lead to decomposition. A similar reaction is observed when $Ru_2(CH_2SiMe_3)_6$ is reacted with ^tBuLi at -80°C, a rapid colour change from green to red occurs, the $^{13}C['H]$ n.m.r spectrum of the red oil obtained contains a sharp singlet at δ + 287 ppm.

Both of the hexa-alkyls react rapidly with carbon monoxide at ambient temperatures and atmospheric pressure. Thus a sample of $Ru_2(CH_2SiMe_3)_6$ dissolved in hexane changes colour from green to cherry red when dry carbon monoxide is passed over the solution. The solution i.r at this stage shows a strong bond at 1690 cm^{-1}. Continued exposure to CO eventually gives an orange solution the i.r spectrum of which contains a strong band at 1665 cm^{-1}.

The intense purple colour of a solution of $Ru_2(CH_2CMe_3)_6$ in hexane is rapidly discharged when dry CO is passed over it, becoming very pale yellow within five minutes, no intermediate stage is visible. The solution i.r. spectrum shows at least seven bands in the region 1950-2100 cm^{-1}, the most intense being at 1990 cm^{-1}.

More work is needed to characterise these products fully, it is tempting to speculate that the initial cherry red product formed from $Ru_2(CH_2SiMe_3)_6$ contains a bridging carbonyl group, this has been observed previously for an analogous triply bonded molybdenum dimer (88). The only evidence supporting this is that

when the red solution is exposed to vacuum the colour reverts to green, presumably via removal of carbon monoxide. The final products obtained from the two hexa-alkyls are different, whereas that from $Ru_2(CH_2CMe_3)_6$ contains bridging carbonyls, that derived from $Ru_2(CH_2SiMe_3)_6$ resembles more closely an acyl species.

The alkyls also react readily with ^tBuNC to give mononuclear products, with diphenylacetylene to give bright orange products and with NO to give a red solid with a strong band in the i.r at 1825 cm^{-1}.

CHAPTER 4

DIRUTHENIUM TETRAACETATE

DIRUTHENIUM TETRAACETATE

INTRODUCTION

The reaction between $Ru_2(O_2CMe)_4Cl$ and Grignard reagents proceeds via a disproportionation reaction, the evidence for this was set out in chapter 1. One product is the previously mentioned dimeric Ru (III, III) alkyl, the other is diruthenium tetraacetate, $Ru_2(O_2CMe)_4$.

Whilst binuclear tetracarboxylates are well known and have been extensively studied for many of the transition metals (89) ($M_2(O_2CR)_4$, M = Cr, Mo, W, Rh; $M_2(O_2CR)_4X_2$ M = Os, Re) there was previously no such ruthenium species known, despite many attempts to isolate it.

That this molecule has remained elusive is surprising for two main reasons. Firstly extensive theoretical calculations based on $Ru_2(O_2CH)_4$ by Norman et al (90) have shown conclusively that such species should be stable. Secondly ever since the isolation of the $Ru_2(O_2CR)_4Cl$ compounds numerous electrochemical studies (91) have shown that one electron reductions occur readily in solution presumably generating Ru_2^{4+} species, this has also been observed for $Ru_2(NHCOR)_4Cl$ (92).

Our work has shown that the tetracarboxylate molecule is very stable both in solution and the solid state and can be prepared in varying yields by the action of a range of one electron reducing agents on ruthenium acetate chloride. The route which consistently gives the best yields goes via the "blue reduced ruthenium solutions" (93). This route has been utilized to prepare several analogues containing

a $Ru_2(O_2CR)_4$ core

Discussion

The tetraacetate was first produced by the reaction of $(CH_3)_3Si\ CH_2\ Mg\ Cl$ on ruthenium acetate chloride in thf , the Grignard reagent presumably acting as a soluble one electron reducing agent. Subsequent work has shown it to be formed in all such alkylation reactions.

Satisfactory elemental analyses could not be obtained on the solvated species $Ru_2(O_2CMe)_4\ 2S$ (S = solvent) presumably due to partial loss of solvent, good analyses could be obtained on the naked core $Ru_2(O_2CMe)_4$, easily obtained by exposing the compound to vacuum.

Coordinated thf is discernable in the i.r. spectrum which also shows two characteristic acetate bands ν_{assym} at 1560 cm^{-1} and ν_{sym} at 1440 cm^{-1}. These bands are relatively insensitive to the presence of coordinated solvent, coming at 1550 cm^{-1} and 1440 cm^{-1} in the unsolvated complex.

This facile loss of solvent also necessitated that the crystal used for x-ray diffraction studies was sealed under an atmosphere of argon saturated with thf.

The molecular structure is shown in Figure 9 , the important bond angles and lengths are collected in Table 10. The Ru-Ru bond length is 2.26 Å, this is in good accordance with a bond order of two, lying between those found for the other structurally characterised

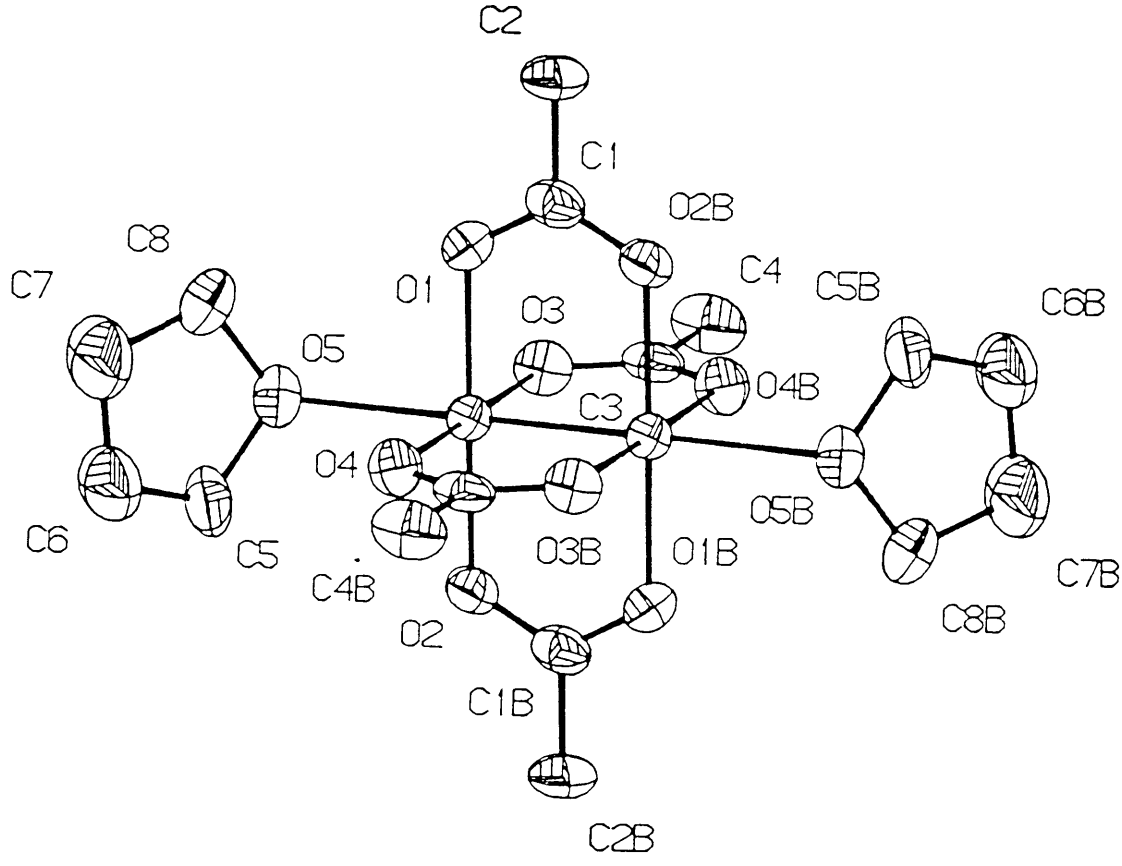


FIGURE 9: MOLECULAR STRUCTURE OF $Ru_2(O_2CMe)_4 \cdot 2THF$

TABLE 10: SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR $Ru_2(O_2CMe)_4 \cdot 2THF$

O(1)-Ru(1)	2.060(5)	O(2)-Ru(1)	2.063(5)
O(3)-Ru(1)	2.061(5)	O(4)-Ru(1)	2.057(5)
O(5)-Ru(1)	2.391(6)	Ru(1)-Ru(1a)	2.261(3)
C(1)-O(1)	1.255(8)	C(3)-O(3)	1.264(7)
C(5)-O(5)	1.444(9)	C(8)-O(5)	1.432(9)
C(2)-C(1)	1.502(10)	C(4)-C(3)	1.482(9)
C(6)-C(5)	1.508(12)	C(7)-C(6)	1.446(14)

O(2)-Ru(1)-O(1)	179.4(1)	O(3)-Ru(1)-O(1)	89.2(2)
O(3)-Ru(1)-O(2)	90.9(2)	O(4)-Ru(1)-O(1)	91.0(3)
O(4)-Ru(1)-O(2)	88.9(2)	O(4)-Ru(1)-O(3)	179.5(1)
O(5)-Ru(1)-O(1)	89.2(2)	O(5)-Ru(1)-O(2)	91.4(2)
O(5)-Ru(1)-O(3)	92.7(2)	O(5)-Ru(1)-O(4)	87.8(2)
C(1)-O(1)-Ru(1)	118.4(4)	C(3)-O(3)-Ru(1)	118.6(5)
C(5)-O(5)-Ru(1)	117.0(4)	C(8)-O(5)-Ru(1)	119.0(5)
C(8)-O(5)-C(5)	107.9(5)	C(2)-C(1)-O(1)	117.7(7)
C(4)-C(3)-O(3)	118.3(7)	C(6)-C(5)-O(5)	105.5(6)
C(7)-C(6)-C(5)	102.7(7)	C(8)-C(7)-C(6)	109.7(8)
C(7)-C(8)-O(5)	107.1(7)		

molecules containing a Ru_2^{4+} core namely $Ru_2(mhp)_4 \cdot CHCl_2$ (2.238 Å), (95) and Ru_2L_2 (2.379 Å) (28), where mhp is the 2-hydroxy-4-methylpyridine anion, and L = tetraza(14)annulene. The bond distance here is also alightly longer than in its closest Ru_2^{5+} analogue (96) $Ru_2(O_2CMe)_4(H_2O)_2\ BF_4$ (ca 0.012 Å), this is consistent with a lower bond order (2 compared with 2.5) due to an extra electron in the antibonding orbital.

Magnetic susceptibility studies both on the solid compound which give μ_{eff} as 2.1 B.M/Ru at 295K and in a 2% hexamethyldisiloxane/thf solution at 305K, which gives μ_{eff} = 2.2 B.M./Ru by the Evans method (97), confirm the paramagnetism of the molecule and indicate the presence of two unpaired electrons.

Thus the structural and magnetic data are in accord with an $\sigma^2\ \pi^4\ \delta^2\ \delta^{*1}\ \pi^{*3}$ electronic configuration proposed in the previously cited theoretical study. An energy level diagram of this scheme, together with that for $Ru_2(O_2CH)_4^+$ for comparison is shown in Figure 10. The electronic structure of $Ru_2(O_2CR)_4Cl$ was mentioned in Chapter 1, for this species the ordering of the π^* and δ^* orbitals is the reverse of what might have been expected on the basis of calculations for the isoelectric Re_2^{4+} system (98); but this order has been established on the basis of independent calculations (99), and is in accordance with the experimentally observed three unpaired electrons.

The pattern of energy levels for $Ru_2(O_2CH)_4$ is qualitatively similar to that for $Rh_2(O_2CH)_4$(100), with the δ^* orbital being the highest occupied orbital followed by the π^*. The important difference, and probably the most significant feature in determining the electronic configuration of the $Ru_2(O_2CR)_4$

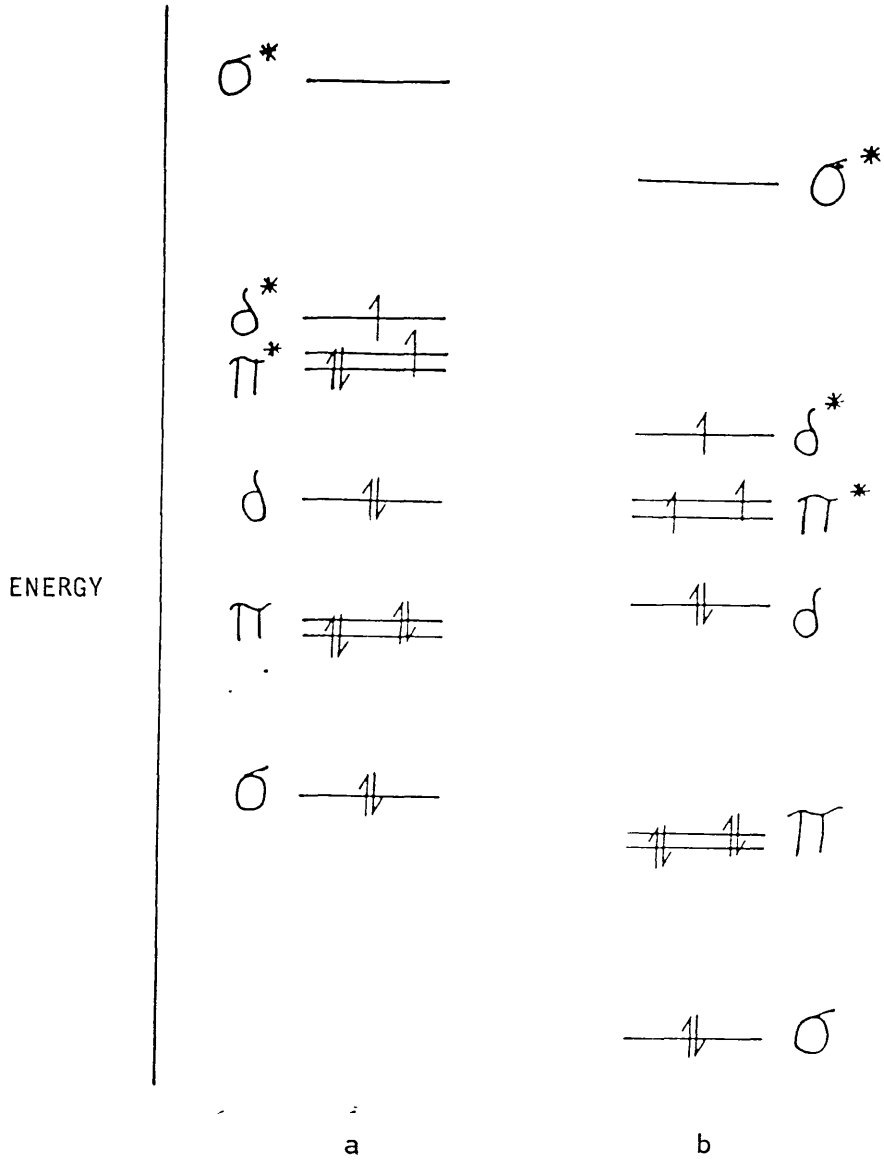


FIGURE 10 : ELECTRONIC CONFIGURATIONS OF

a) $Ru_2(O_2CH_4)$, $\sigma^2\pi^4\delta^2\pi^*3\delta^*1$

b) $Ru_2(O_2CH_4)^+$, $\sigma^2\pi^4\delta^2\pi^*2\delta^*1$

species is that these two levels are so close together so as to be practically degenerate and thus the observed electronic configuration with two unpaired electrons is attained (in preference to $\sigma^2 \pi^4 \delta^2 \pi^{*4}$ for example). This theoretical prediction is now supported by the experimental observations made on $Ru_2(O_2CMe)_4$. The observed stability of this system has invalidated all previous conjecture as to why the $Ru_2(O_2CR)_4$ species were unobtainable, some of these arguments were based on electronic configuration.

Complimentary experimental evidence for two unpaired electrons comes from the ready reaction of this species with one electron radicals such as nitric oxide which gives the red neutral diamagnetic adduct $Ru_2(O_2CMe)_4 \cdot 2NO$.

Despite this obvious paramagnetism, no E.P.R. spectrum could be observed, even in a 2-methyl-tetrahydrofuran glass at 77K. This may be due to large zero-field splitting arising from strong dipole-dipole interactions between the unpaired electrons in the assumed triplet ground state.

Cyclic voltametry studies in 0.2M $Bu^N_4 NPF_6$-thf or acetonitrile solutions show a single facile one electron oxidation, (Table II). The oxidation potential is much more negative in 0.2M Bu^N_4NCl thf solution, in this case the species being oxidised is probably $Ru_2(O_2CMe)_4Cl_2^{2-}$ for which oxidation should occur much more readily than for its neutral precursor.

Reactions of $Ru_2(O_2CMe)_4$

Reactions involving exchange of bridging group, or terminally bound

TABLE 11 CYCLIC VOLTAMMETRY OF $Ru_2(O_2CMe)_4$.

$E^{\frac{1}{2}}$ (v)[a]		
MeCN[b]		thf[c]
0.00 (-1.84)	-0.45[d]	-0.05

a - All $E^{\frac{1}{2}}$ values measured at 295K, referenced with respect to a saturated calomel electrode at which ferrocene is oxidised at +0.34v.

b - electrolyte solution, 0.2M $Bu^N_4 NPF_6$ in acetonitrile.

c - electrolyte solution, 0.2M $Bu^N_4 NPF_6$ in thf

d - electrolyte solution, 0.2M Bu^N_4 NCL in acetronitrile reversible redox couple Ru_2^{4+} / Ru_2^{5+} (irreversible reduction.)

ligands, and cleavage reactions have been described elsewhere (14). The reaction with alkyl grignard reagents leads to decomposition in the majority of cases, no ruthenium alkyls could be isolated. In an attempt to generate alkylate anions such as $Li_2Ru_2R_6$ the reaction of $Ru_2(O_2CMe)_4$ and methyllithium was studied both with and without adding tetramethylethylenediamine (TMEDA) decomposition occurred below room temperature in both cases.

The only successful alkylation was that using mesitylmagnesiumbromide (mesityl = 2,4,6 trimethylphenyl). The reaction between this Grignard reagent and $Ru_2(O_2CMe)_4$ in thf at -80°C, gives a deep red solution on warming to room temperature. This red, air sensitive compound is insoluble in aliphatic hydrocarbons, but is soluble in aromatic hydrocarbons, diethyl ether and dichloromethane. The i.r. spectrum shows the complete removal of acetate groups and the presence of aromatic ligands. Further spectroscopic characterisation is difficult since although it is apparently paramagnetic (giving broad n.m.r. signals) like the parent acetate it is E.P.R. silent. Elemental analyses indicate the stoichiometry as $Ru_2(mesityl)_4$, molecular weight determination (cryoscopically in benzene) gives a high value ca 740, compared with the expected 678, because no accurate molecular weight is known, accurate magnetic succeptibility measurements are not possible.

CATALYSIS BY DIRUTHENIUM TETRAACETATE

This section deals with the activity of the title compound towards alkene hydrogenation. It contains only brief details of preliminary studies, since which time the work has been extended by others (101), more comprehensive results will be reported elsewhere.

Various ruthenium acetate compounds have previously exhibited this kind of catalytic behaviour. The oxo-centred ruthenium acetate trimer, $Ru_3O(O_2CMe)_6(H_2O)_3^+ O_2CMe^-$ in dimethylformamide at 80°C will catalyse the reduction of alkenes (102). Mechanistic studies have shown that only one ruthenium centre is active, coordinating both hydrogen and alkene and mediating the subsequent hydride transfer. Other catalysts can be prepared from the oxo-centred acetate, but do not retain the tri-ruthenium core. Both $Ru_2(O_2CMe)_4Cl$ and the triphenylphosphine adduct exhibit catalytic activity (103), but only in the presence of strong non coordinating acids and excess phosphine, in both cases the active species is reported to be $Ru(PPh_3)(alkene)^{2+}$ (22). Present studies have shown methanolic solutions of $Ru_2(O_2CMe)_4$ will catalyse the reduction of terminal and cyclic mono alkenes and terminal alkynes homogeneously at room temperature under atmospheric pressure of hydrogen. Similar reductions can be afforded in ethanol or dimethylformamide, but activity is greatly reduced in acetonitrile or dichloromethane and none is observed in thf or benzene. This reduction occurs with negligible alkene isomerization. This system is not active for the hydrogenation of internal alkenes, dienes, trans alkenes or for carbonyl (C=O) or imine (C=N) functionalities. (Table 12).

Studies made under standard conditions (of H_2 pressure and olefin concentration) indicate the reactivity decreases in the order.

Cyclic alkene > terminal alkene > terminal alkyne

measurement of initial H_2 uptake seems to indicate that the reaction is first order with respect to alkene, at low alkene concentrations, for a range of substrates in a variety of solvents. Representative plots

TABLE 12 HYDROGENATION OF ALKENES WITH $Ru_2[O_2CMe]_4$ [a]

SUBSTRATE	TIME (minutes) [b]
HEX-1-ENE	70
OCT-1-ENE	85(96) [c]
CYCLOHEXENE	63
CYCLOOCTENE	79(300) [c]
STYRENE	125
HEX-1-YNE	570
OCT-1-ENE	94 [d]
OCT-1-ENE	90 [e]
OCT-1-ENE	340 [f]

a - reaction conditions: 50 cm^3 of 2mmol methanolic solution of catalyst, 25°C, 1 atm, catalyst: substrate 1:15.

b - time for complete hydrogenation.

c - time for complete hydrogenation using $[Rh_2(O_2CMe)_4]$ under identical conditions.

d,e,f - solvent ethanol, DMF, acetonitrile respectively.

are shown in Figure 11. Total hydrogen consumption levels off close to that required for complete hydrogenation of the alkene.

In the absence of alkene, $Ru_2(O_2CMe)_4$ will react with hydrogen, indicated by a change in the visible spectrum (Figure 12). It has not proved possible to characterise this hydride species by ^1H n.m.r spectroscopy as it is paramagnetic, attempts to isolate it as a solid also failed, any reduction of volume of solutions containing the hydride led only to the precipitation of the tetra-acetate.

For the ruthenium oxo centred trimer and $Rh_2(O_2CMe)_4$ an equilibrium such as that shown below has been postulated (104).

$$M_2(O_2CMe)_4 + H_2 \rightleftharpoons M_2(O_2CMe)_3H + H^+ + {}^-O_2CMe$$

Additional evidence that this is the type of activation step in the present case is two-fold, firstly one mole of H_2 is consumed per dimer, and secondly addition of free acetate ions (as sodium or lithium acetate) supresses gas uptake.

Similarly in the absence of H_2, $Ru_2(O_2CMe)_4$ will react with alkenes, again shown by the visible spectrum (Figure 13). This change in the visible spectrum cannot be observed using the analogous rhodium acetate, but can be seen when $Rh_2(O_2CCF_3)_4$ is used, this latter system is postulated to give a 1:1 adduct with alkenes. In the present case it has not proved possible to isolate adducts with any of the alkenes used as substrates for hydrogenation studies nor with ethylene. However tetracyanoethylene will react in ether to give an air stable red powder, the infra red spectrum of which indicates the presence of both acetate and alkene groups, but the stoichiometry is not known.

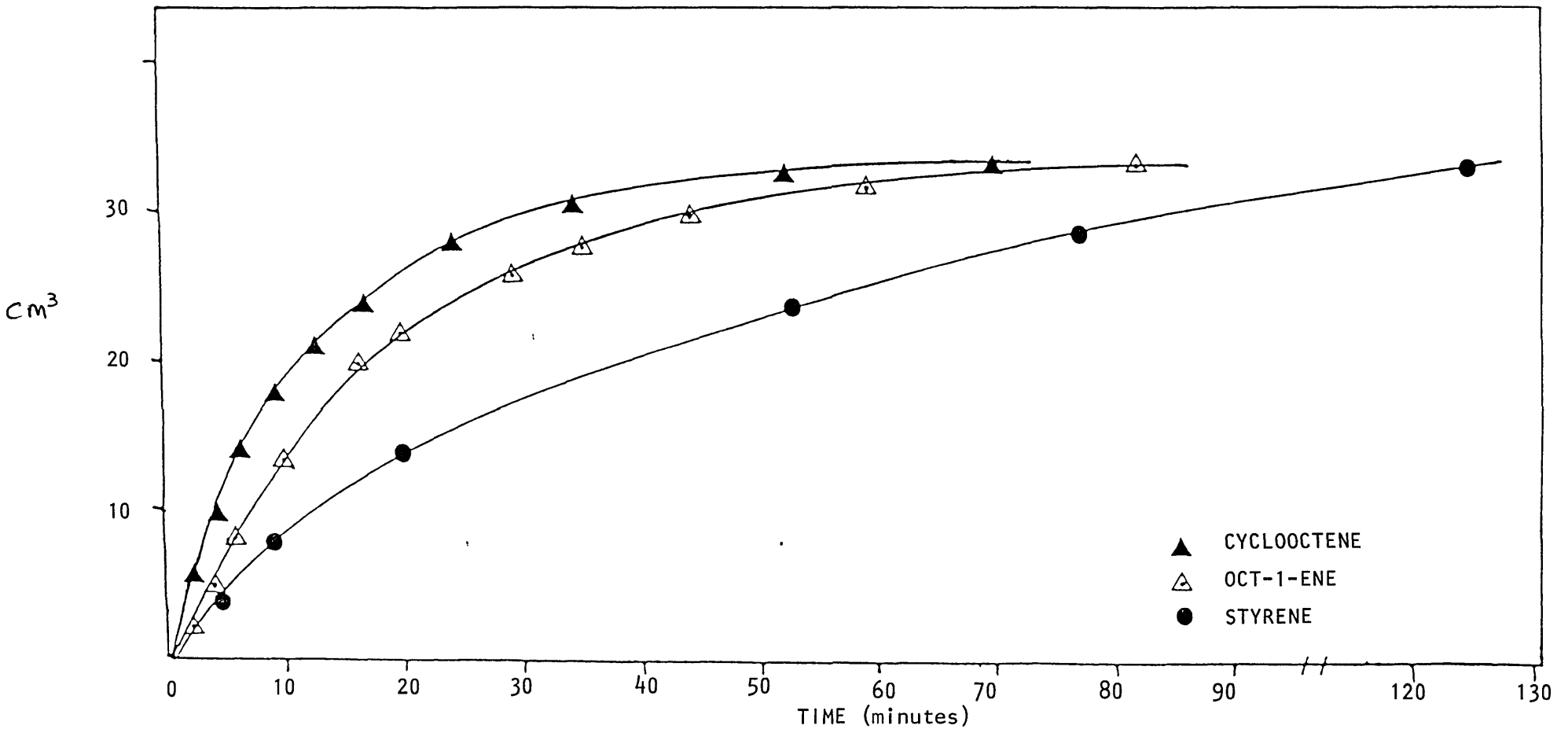


FIGURE 11: Representative hydrogen consumption plots for the $Ru_2(O_2CMe)_4$ catalysed hydrogenation of alkenes in methanol at 1 ATM hydrogen pressure and 25°C (50 cm^3 methanol, 0.1mM $Ru_2(O_2CMe)_4$, 1.5mM alkene)

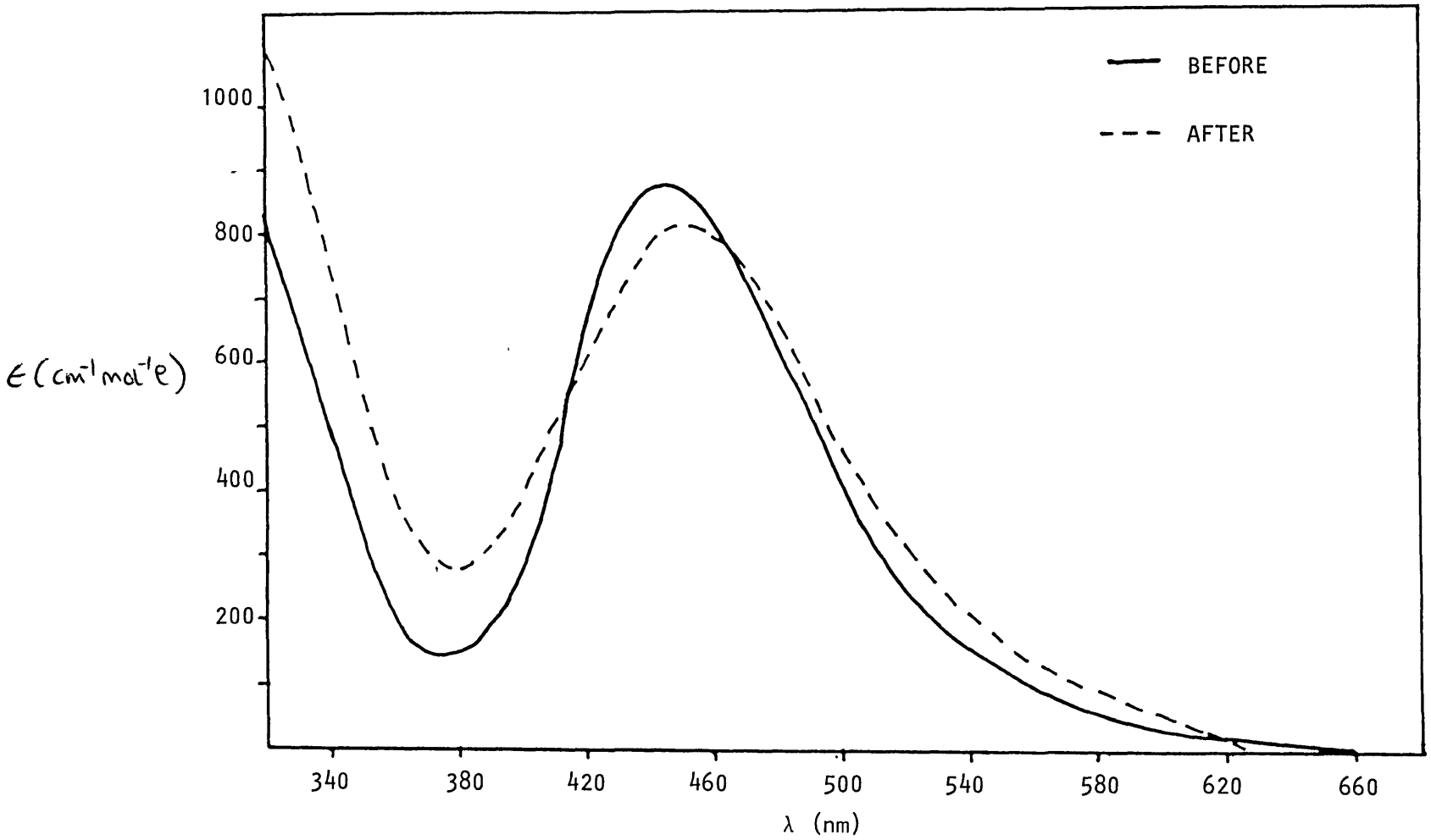


FIGURE 12: Change in electronic spectrum of a methanolic solution of $Ru_2(O_2CMe)_4$ after stirring under hydrogen (1 ATM) for 1 hour.

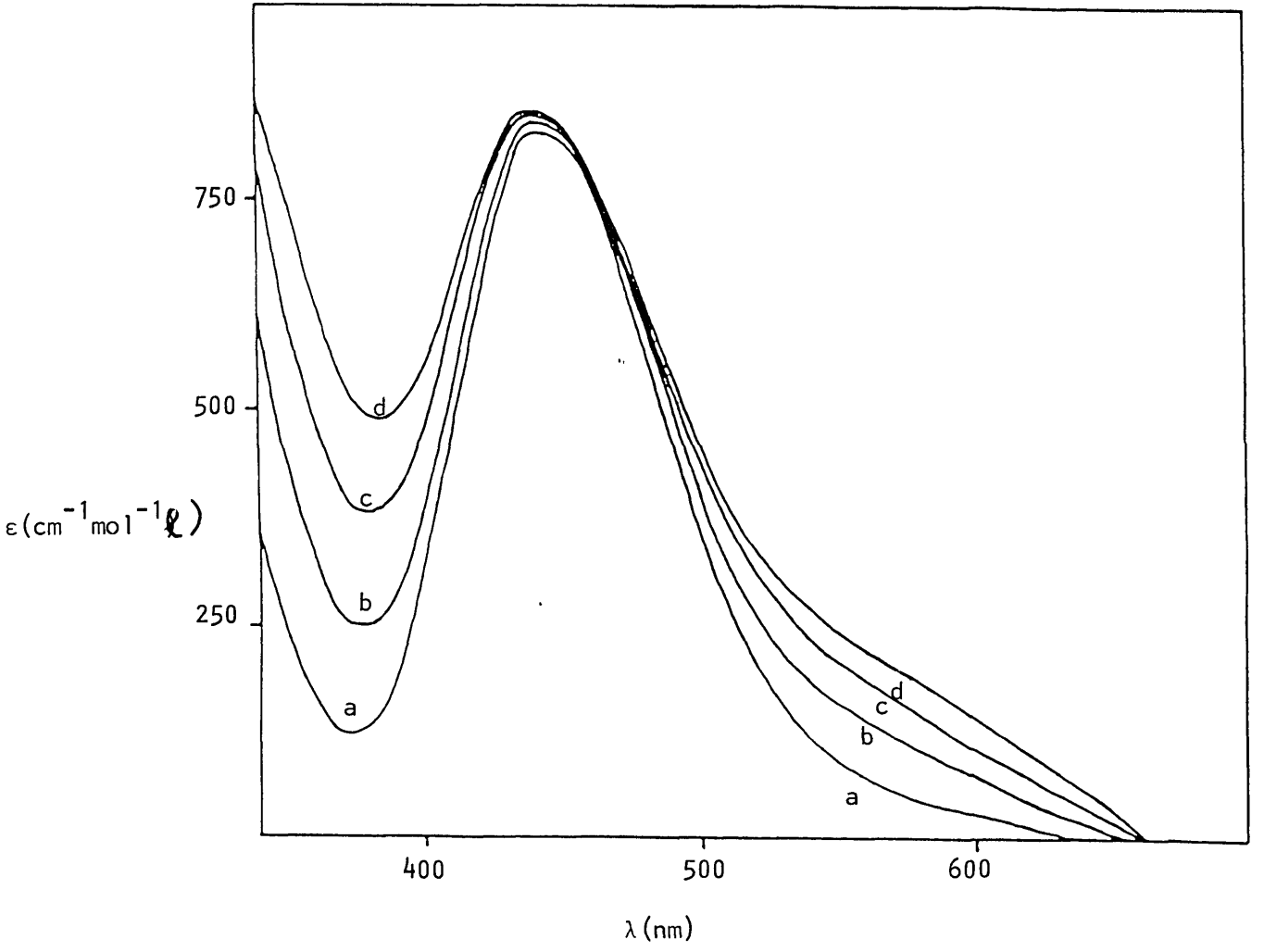


FIGURE 13: Changes in Electronic spectrum accompanying sequential addition of Oct-1-ene to $Ru_2(O_2CMe)_4$ (3 cm^3 of a 0.9 mM solution in methanol) at 25°C.

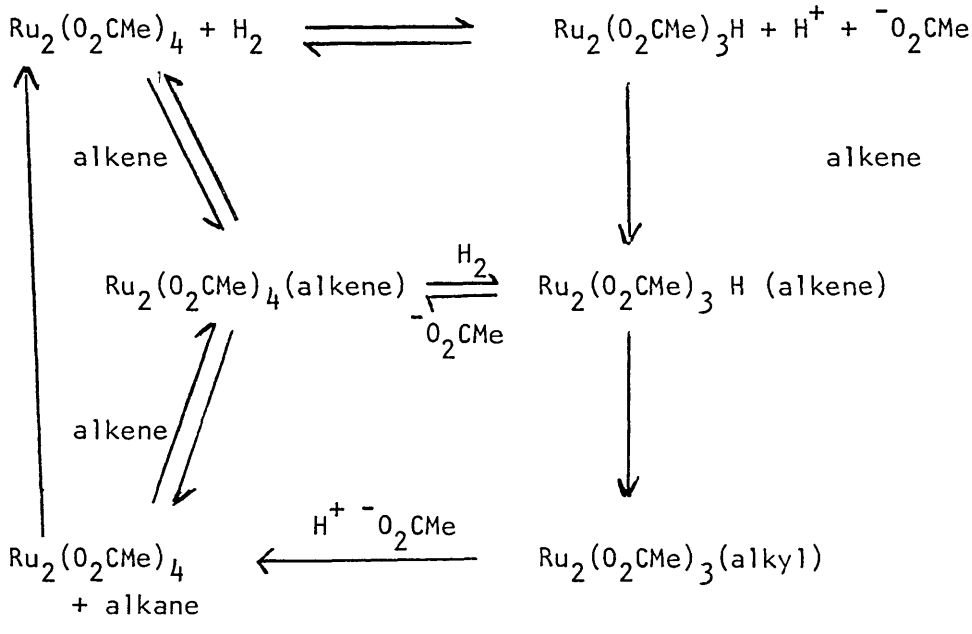
a) No oct-1-ene present

b) $Ru_2(O_2CMe)_4$: Oct-1-ene molar ratio 1 : 500

c) 1 : 900

d) 1 : 1400

Although detailed mechanistic studies have not been carried out, in view of the observations reported above, (with regard to H_2 uptake, and reaction between the metal complex and alkene and olefin), and in the light of the published work, a tentative mechanism can be postulated.



The initial activation of H_2, and coordination of alkene has been referred to above, the subsequent alkene insertion into the metal-hydride bond is well precedented(50). The small degree of isomerization observed probably means that alkyl formation is not reversible, this low degree of isomerization compares favourably to that obtained using $Rh_2(O_2CMe)_4$ (>15%). Although it is fairly robust (the catalyst can be reclaimed almost quantitavely following single hydrogenation experiments) unlike the very sensitive ruthenium oxo alkyl, discussed in Chapter 3, its air sensitivity and high cost are likely to limit its potential utility.

EXPERIMENTAL

The apparatus used for these hydrogenation studies was similar to

that previously reported (105), u.v-visible spectra were recorded on a Perkin Elmer 551 spectrophotometer, hydrogen was purified by passage through an Englehardt deoxo catalyst, all other manipulations were carried out under argon or in vacuo . All solvents and alkenes were distilled under argon and degassed prior to use.

Isomerised olefins and alkanes were analysed by gas chromatography using a Perkin Elmer Sigma 1B gas chromatographic system, the conditions used were as follows:

Column : 4 metre column of 15% carbowax 20m on Chromasorb (W80-10 mesh).

Detector : Flame Ionization Detector.

Injection Temperature : 130°C

Oven Temperature : 70°C

Detection Zone Temperature : 80°C

Typical separations achieved are given below in terms of retention times (RT).

COMPOUND	RETENTION TIME / MINUTES
Cyclohexane	2.37
Hept-3-ene	2.43
Octane	3.06
Cyclohexene	3.46
Oct-1-ene	3.88
Methanol	5.36

CHAPTER 5

PALLADIUM, RUTHENIUM AND RHODIUM PHOSPHINE ALKYL COMPOUNDS.

PALLADIUM, RUTHENIUM AND RHODIUM PHOSPHINE ALKYL COMPOUNDS.

INTRODUCTION

This final chapter is concerned with the interaction of the binuclear acetates of ruthenium and rhodium, $Ru_2(O_2CMe)_4Cl$ and $Rh_2(O_2CMe)_4$ with alkylating agents in the presence of dmpe , and that between $Pd(O_2CMe)_2$ and alkylating agents in the presence of both dmpe and PMe_3

PART 1 - PALLADIUM COMPOUNDS.

INTRODUCTION

Even within the illustrious platinum group metals, palladium and its compounds exhibit outstanding catalytic versatility, being active for alkene oxidation, oligomerization, carbonylation, vinylation, acetoxylation, isomerization, and for the hydrogenation not only of alkenes but also of dienes and alkynes.

Intermediates with carbon-palladium σ bonds are often implicated, and because of this any study of compounds containing such bonds may prove valuable.

Divalent palladium organometallic compounds are less stable towards air and moisture than their platinum (II) analogues. As is true of all such compounds their stability depends on both the alkyl groups and the neutral ligands. Although compounds containing elimination stabilized alkyls, or metallocyclic rings are more stable, ethyl and propyl compounds are known (106). Similarly the presence of strongly σ-donating and/or π accepting ligands have a stabilizing influence.

However, in the context of present work reports of reactions not involving ancillary ligands are more interesting. The only reported palladium (II) compound containing exclusivley Pd-C σ bonds is $[Pd(C_6F_5)][NBu^n_4]_2$(107). In the majority of cases such interactions lead to decomposition exemplified by that between palladium dichloride and ethyl Grignard (109).

$$2\ Et\ Mg\ Br + Pd\ Cl_2 \longrightarrow C_2H_6 + C_2H_4 + 2\ Mg\ Cl\ Br + Pd$$

The interaction of palladium (II) acetate with lead, tin and mercury alkyls has been reported by Heck(109). The intermediate alkylpalladiumacetates were not isolated but used in situ to alkylate alkenes.

We have attempted similar reactions, that between Me_3SiCH_2MgCl and palladium (II) acetate in diethyl ether at -80^oC gives an intense red solution. If the volatile materials are removed under reduced pressure whilst keeping the temperature below -40^oC, the residue can be extracted at -78^oC with hexane, generating a red solution. Attempts to characterize the products were unsuccessful as the compound decomposes rapidly above -40^oC (within two minutes). Similar observations were made using all other simple Grignard reagents.

Stable products could only be obtained in the presence of phosphines. Divalent palladium phosphine alkyl compounds have been prepared by a variety of methods, these can be broadly divided into two categories a) from zero valent palladium complexes by oxidative addition or by nucleophilic attack on alkene complexes, b) from

divalent palladium complexes either by insertion into pd-X bonds (x = halide or hydride) or by direct alkylation of L_2PdX_2. The latter is the classical route, being the one employed to prepare the first organometallic palladium complexes (110).

The synthetic route used in this present work falls into the latter category. As mentioned above the divalent starting material used was palladium (II) acetate, a brown powder formed by dissolving palladium sponge in acetic acid containing a little nitric acid. It is trimeric in the solid state and in benzene at 37°C, but dissociates to give monomers at 80°C (111).

DISCUSSION

Interaction of Palladium (II) acetate in thf containing excess PMe_3 or three equivalents of dmpe with MgR_2 or RMgCl gives the cis alkyls $PdR_2(PMe_3)_2$ (R = Me, CH_2CMe_2Ph) and PdR_2(dmpe) (R = Me, CH_2CMe_2Ph, CH_2SiMe_3, CH_2Ph) and the trans alkyls $PdR'_2(PMe_3)_2$ (R' = CH_2SiMe_3, CH_2Ph). All of the compounds are air sensitive and soluble in hydrocarbons. The assignment of cis or trans stereochemistry is based on ^1H and ^{31}P ^1H nmr spectroscopy. The nmr data are collected in Table 12, elemental analytical data and molecular weights are collected in Table 13.

a) Trimethylphosphine Complexes

Compounds of the type cis $PdMe_2(PR_3)_2$ are known (106a) and cis $PdMe_2(PMe_3)_2$ has previously been reported, but no n.m.r or experimental details were given (112). The compound cis $PdMeI(PMe_3)_2$ has been made from $Pd(PMe_3)_4$ (113).

The only known trimethylsilylmethyl compounds are cis $PdR_2(PEt_3)_2$ and trans $PdCl\ R\ (PEt_3)_2$ (114). There are a wide range of other compounds of the stoichiometry PdR_2L_2 which contain palladium carbon σ bonds .

b) 1,2,bis(dimethylphosphino)ethane complexes

These compounds are all necessarily cis, no dmpe compounds are known, but compounds containing other chelating phosphines have been reported (116) . Attempts to prepare compounds using diphenylmagnesium or allyl magnesium bromide were unsuccessful, leading to the formation of the known $Pd(dmpe)_2$ (117) and biphenyl in the first case, and a mixture of organic products in the second.

No cyclometallation has been observed at room temperature, for either the PMe_3 or dmpe compounds, no neopentyl compound could be isolated. Palladium metallacycles containing dppe have been reported (14). The ^1H n.m.r assignments are straightforward, with the exception of those peaks due to the alkyl methylene protons. For the cis isomers the multiplicity of these resonances arises from coupling with two magnetically inequivalent phosphorus nuclei (cis and trans) which gives a second order spectrum,. characteristic of an $AA'MM'X_2'X_2$ spin system, (118) their overall appearance depending on the magnitude of the two coupling constants.

c) ACETATE COMPLEXES

The reaction between palladium acetate and a tertiary phosphine is not unprecedented, such an interaction using triphenylphosphine has been reported to give $Pd(O_2CR)_2L_2$ containing unidentate acetate groups (14). The i.r. spectrum of the PMe_3 compounds shows a very

strong band at 1610 cm^{-1}, the dmpe compound one at 1625 cm^{-1}, compared with 1634 cm^{-1} in the triphenylphosphine compound, all falling in the region indicative of unidentate acetates.

Divalent palladium has been categorised by Chatt as a class B metal (119),(analagous to a Pearson soft acid), and as such the reaction displacing a "hard" O-bonded ligand with a "soft" tertiary phosphine ligand is facile, with the chelating phosphine prolonged reaction times lead to formation of $Pd(dmpe)_2$.

This oxidation state is by far the most important for palladium, these compounds are generally square planar and diamagnetic (this is in contrast to Ni(II) complexes which are predominantly octahedral and paramagnetic). Thus although higher coordination numbers are known <u>trans</u> bis(acetato)bis(dmpe)palladium (II) is unusual in that it is six coordinate and yet diamagnetic.

Since this is a d^8 system, pure octahedral symmetry should give rise to paramagnetism, as is observed (albeit reduced) in the approximately octahedral PdF_2. More common is a severely tetragonally distorted structure as is found in $PdI_2(diars)_2$[diars= <u>o</u>-phenylenebis(dimethylarsine)]. (120). Such a distortion causes a shift in the relative energy levels of the d-orbitals, until such a point is reached where the pairing energy is less than the energy gap between the two highest orbitals (Figure 14), whereupon the compound becomes low spin. Such a distortion could explain the observed properties of the dmpe compound. The limiting case would be $[Pd(dmpe)_2]^{2+}$. 2 CH_3COO^- but this can be ruled out both on conductivity and ^1H nmr data, the latter indicating bound, unidentate acetate ligands, rather than free ions, the infra-red spectrum is

corroborative evidence.

Another alternative is that different species exist in the solid state and solution with dissociation occuring to give $Pd(O_2CMe)_2(dmpe)$, molecular weight studies were inconclusive, but the absence of free dmpe in the ^{31}P n.m.r seems to rule this out.

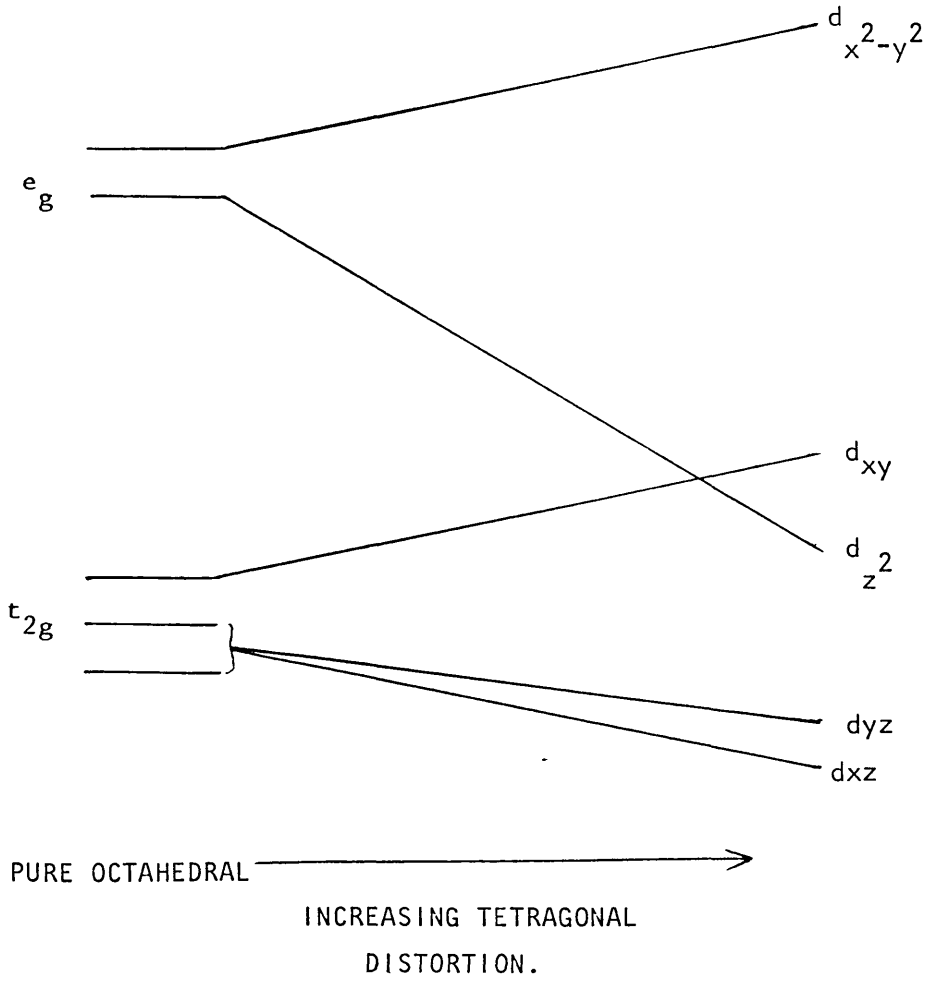


FIGURE 14: Energy level diagram showing the increased splitting of d orbitals as an octahedral set of ligands becomes tetragonally distorted.

TABLE 13 NUCLEAR MAGNETIC RESONANCE DATA FOR PALLADIUM COMPOUNDS

COMPOUND	CHEMICAL SHIFT, δ.	
	^{1}H, J(Hz)	$^{31}P\{^{1}H\}$
1. cis-$PdMe_2(Me_3)_2$	0.74d(6,Pd-Me), $^{3}J_{PH}$=3.3	-22.4s
	0.93d(18,PMe_3), $^{2}J_{PH}$=5.8	
2. trans-$Pd(CH_2SiMe_3)_2(PMe_3)_2$	0.31s(18,CH_2SiMe_3)	-15.5s
	1.09"t"(18,PMe_3), $^{2}J_{PH}+^{4}J_{PH}$ = 6.0	
	-0.25t(4,CH_2SiMe_3) $^{3}J_{PH}$ = 8.3	
3. cis-$Pd(CH_2CMe_2Ph)_2(PMe_3)_2$	0.69d(18,PMe_3), $^{2}J_{PH}$ =5.8	-32.8s
	1.10s(4,CH_2CMe_2Ph)	
	1.71s(12,CH_2CMe_2Ph)	
	7.00-7.80m(10, CH_2CMe_2Ph)	
4. trans-$Pd(CH_2Ph)_2(PMe_3)_2$	1.00"t"(18,PMe_3), $^{2}J_{PH}+^{4}J_{PH}$ = 6.6	-12.0s
	2.60t(4,CH_2Ph), $^{3}J_{PH}$ = 7.6	
	7.00-7.60m(10,CH_2Ph)	
5. cis-$Pd(CH_2SiMe_3)_2$dmpe	0.34s(18,CH_2SiMe_3)	23.44s
	0.53m(4,CH_2SiMe_3)	
	0.89d(12,Me_2-P), $^{2}J_{PH}$= 8.1	
	0.86d(4,CH_2-P), $^{2}J_{PH}$= 13.4	

6. cis-$Pd(CH_2CMe_2Ph)_2$dmpe	0.55d(12,$\underline{Me}_2$-P), $^2J_{PH}$ =7.2	14.12s
	0.74d(4,$\underline{CH}_2$-P), $^2J_{PH}$ = 12.5	
	1.76s(12,CH_2-$C\underline{Me}_2Ph$)	
	2.16"q"(4,$\underline{CH}_2$-CMe_2Ph)	
	7.03-7.29m 7.74-7.85m } (10,CH_2-$CMe_2\underline{Ph}$)	
7. cis-$PdMe_2$dmpe	0.81"t"(6,Pd-$\underline{Me}$)	20.14s
	0.92d(12,P$\underline{Me}_2$), $^2J_{PH}$= 8.0	
	0.98s(2,$\underline{CH}_2$-P)	
8. cis-$Pd(CH_2Ph)_2$dmpe	0.59d(12,$\underline{Me}_2$-P), $^2J_{PH}$ = 8.3	20.87s
	0.68d(4,$\underline{CH}_2$-P), $^2J_{PH}$= 16.17	
	3.11"q"(4,$\underline{CH}_2Ph$)	
	6.91-7.41m(10,CH_2-$\underline{Ph}$)	
9. trans $Pd(O_2CMe)_2(PMe_3)_2$[6]	0.12s(18,P$\underline{Me}_3$)	
	0.47s(6,$O_2C\underline{Me}$)	
10. trans $Pd(O_2CMe)_2(dmpe)_2$[c]	2.38m(8,$\underline{CH}_2$-P)	46.60s[d]
	1.53s(6,$O_2C\underline{Me}$)	
	1.31s(24,P$\underline{Me}_2$)	

a. All spectra in C_6D_6 at 25°C unless otherwise stated.

b. In $CDCl_3$ at 25°C.

c. In $CDCl_3$ at 25°C.

d. In $CHCl_3$, with 10% $CDCl_3$.

TABLE 14 ANALYTICAL DATA FOR PALLADIUM COMPOUNDS

COMPOUND	m.p.,θ/°C	FOUND (REQUIRED)%			
		C	H	P	M
1. cis-$PdMe_2(PMe_3)_2$	84-6	33.4 (33.3)	8.4 (8.3)	21.2 (21.5)	270 (288)
2. trans-$Pd(CH_2SiMe_3)_2(PMe_3)_2$	81-2	38.4 (38.5)	9.2 (9.2)	13.8[a] (14.3)	420 (432)
3. cis-$Pd(CH_2CMe_2Ph)_2(PMe_3)_2$	80-1	59.5 (59.5)	8.4 (8.4)	11.6 (11.8)	510 (524)
4. trans-$Pd(CH_2Ph)_2(PMe_3)_2$	98	54.2 (54.5)	7.2 (7.3)	14.0 (14.1)	428 (440)
5. cis-$Pd(CH_2SiMe_3)_2$dmpe	77-80	39.1 (39.0)	8.9 (8.9)	14.4[b] (14.4)	420 (430)
6. cis-$Pd(CH_2CMe_2Ph)_2$dmpe	118-121d	59.3 (59.7)	8.1 (8.1)	11.9 (11.8)	510 (523)
7. cis-$PdMe_2$dmpe	128-131	33.6 (33.5)	7.6 (7.7)	21.6 (21.6)	270 (286)
8. cis-$Pd(CH_2Ph)_2$dmpe	98-101d	54.9 (54.7)	6.9 (6.9)	14.3 (14.1)	425 (439)
9. trans $Pd(O_2CMe)_2(PMe_3)_2$	157	31.5 (31.9)	6.3 (6.4)	16.4 (16.5)	350 (376)
10. trans $Pd(O_2CMe)_2$(dmpe)$_2$	252-254	36.2 (36.8)	6.8 (6.9)	23.4 (23.8)	-

[a]Si 12.7 (12.9) [b]Si 13.0 (12.6)

PART II - RUTHENIUM COMPOUNDS

INTRODUCTION

The interaction of ruthenium acetate chloride with alkylating agents in the presence of trimethylphosphine has been utilized to prepare a range of ruthenium (II) phosphine alkyls and aryls (17). The work described here uses the chelating phosphine dmpe, and comparisons of the products obtained are made. Previously the mechanism of the reduction undergone by ruthenium during these alkylations was unknown, as mentioned in Chapter 3 it is tempting to postulate this is due to the Grignard reagent acting as a soluble one electron reducing agent in thf.

Similar compounds to those described here have been previously synthesized from $RuX_2Chelate_2$ species (X = halide ,chelate = dmpe, dppe or dppm (121).

DISCUSSION

a) cis dimethyl bis (dmpe) ruthenium (II).

This compound was first prepared by Chatt and Hayter from $RuX_2(dmpe)_2$ (122). No reaction was observed using the Grignard reagent, and trialkylaluminiums give the cis alkyl halide. The cis dichloride can be smoothly alkylated using methyl lithium, but attempts to alkylate the trans isomer led to decomposition. No trans isomer was observed in the present case.

The stereochemistry can be deduced from the $^{31}P['H]$ n.m.r. spectrum,

which consists of two "triplets". The proton spectrum shows a complex multiplet containing at least eight lines centred around δ-0.36 ppm for the methyl group, two broad singlets for the phosphine methyls and a "triplet" for the phosphine methylenes.

b) trans bis(trimethylsilylmethyl)bis(dmpe)ruthenium (II)

Unlike the dimethyl, this compound has trans alkyl groups. Again this assignment is based on the $^{31}P['H]$ n.m.r spectrum, which consists of a sharp singlet whose appearance does not change, when the solution is cooled to $-50^{o}C$.

The 'H and $^{31}P['H]$ n.m.r data are collected in Table 15, the analytical data in Table 16.

The coloured hexane solution obtained from the first extraction of the reaction residues yielded a microcrystalline brown compound. In addition to the sharp singlet due to the trans isomer, the $^{31}P['H]$ n.m.r spectrum also contains two multiplets. These may be due to a cis dialkyl product, but this is a very minor impurity and could not be isolated, making it impossible to identify it directly. However comparison of the $^{31}P['H]$ n.m.r spectrum of this minor product with that of the compound presumed to be the dmpe metallocycle (see Chapter 3) shows them to be the same compound. An analogous reaction with PMe_3 gives a metallocyclic product.

cis bis(neophyl)bis(dmpe)ruthenium (II)

An analogous reaction with $PhMe_2CCH_2MgCl$, gives a yellow air

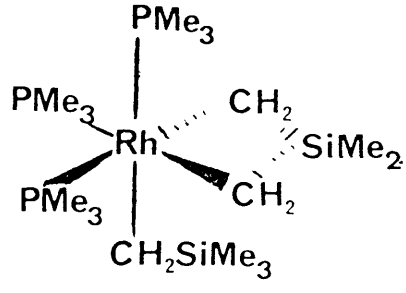
sensitive crystalline solid, whose $^{31}P['H]$ indicates cis disposition of the alkyl groups.

PART III - RHODIUM COMPOUNDS

a) Methyl bis(dmpe)rhodium(I)

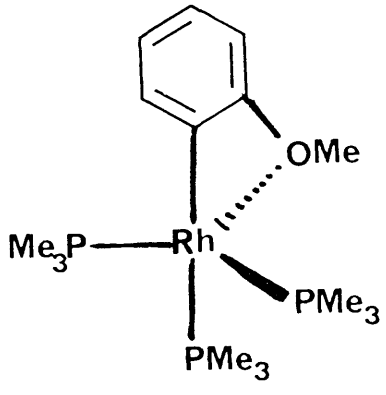
The interaction of dirhodium tetraacetate with one equivalent of dimethylmagnesium in the presence of dmpe gives $Rh(Me)dmpe_2$ in 45% yield. This yellow crystalline very air sensitive compound is soluble in ether or aromatic hydrocarbons, but only slightly soluble in hexane. It has been fully characterised by elemental analyses, mass spectrometry and nuclear magnetic resonance.

The interaction of rhodium acetate with alkylating agents in the presence of PMe_3 has been studied. With alkyl Grignards Rh(III) products are formed, using MeMgCl the product is Fac $RhMe_3(PMe_3)_3$ whilst the reaction with trimethylsilylmethylmagnesiumchloride gives a metallocycle (17a,b)-



The use of aryl Grignard reagents results in the formation of Rh(I) products (17c), thus diphenylmagnesium gives $Rh(C_6H_5)(PMe_3)_3$ which has a distorted square planar structure, the product when using O-methoxy phenylmagnesiumchloride is nominally also four

coordinate, but the authors postulate a distorted five coordinate structure.



The latter compound is much more stable but it is not known if this is a consequence of the increased coordination number.

In the present case it is not possible to assign stereochemistry on the basis of room temperature $^{31}P['H]$ n.m.r. This consists of a doublet centred at δ + 33.7 ppm with J_{P-Rh} = 128 Hz (a value consistent with other observed Rh(I) - phosphorus coupling constants (123)).

The two preferred configurations for five coordinate species are basal square pyramidal (BSP) and trigonal bipyramidal (TBP). The former results in four equivalent phosphorous nuclei, and should give a doublet (split by the rhodium) as observed, but this doublet could also result from fluxionality (common amongst five coordinate species) which would also render all the phosphorus nuclei equivalent.

The distinction can be made with the aid of low temperature n.m.r, whereby the fluxionality is slowed down and discrete structures

become discernable. When a toluene solution of $Rh(Me)(dmpe)_2$ is cooled down to -20°C, the doublet begins to disappear and other signals emerge, these include two prominent doublets of doublets centred at δ + 22 ppm (J_{Rh-P} = 136Hz, J_{P-P}= 16Hz) and a doublet of multiplets centred at δ - 9.1 ppm, other features are less distinct. Attempts to cool the solution below -25°C, led to loss of resolution rather than enhancement, this is probably due to crystallisation of the sample, visible at these temperatures. This seems to suggest that the room temperature doublet is due to fluxionality, and that the low temperature structure is nearer to being TBP than BSP.

In the presence of excess alkylating agent, the reaction yields an orange air sensitive solid, which is very soluble in hexane. The reaction of phosphines with rhodium acetate to give Rh(I) and Rh(III) species is known, in the light of this it is tempting to postulate that this product is a Rh(III) alkyl, (possibly $Rh\,Me_3$ dmpe). The elemental analysis is inconclusive, but shows a lower percentage of phosphorus than in the Rh(I) alkyl indicating the presence of a higher alkyl. The $^{31}P['H]$ spectrum is very complicated, comprising of at least six multiplets, the largest visible coupling constant is 95Hz, if this is due to rhodium-phosphine coupling its magnitude, whilst on the border line is more indicative of Rh(III) than Rh(I). Attempts to purify this compound further have failed.

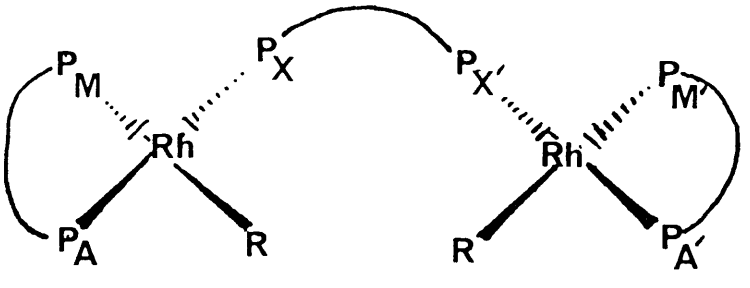
b) Bis(trimethylsilylmethyl)tris(dmpe)dirhodium(I)

The interaction of rhodium(II)acetate with Me_3SiCH_2MgCl in thf at low temperature in the presence of dmpe, gives the title compound

as red air sensitive crystals which are very soluble in hydrocarbon solvents. Elemental analysis gives the stoichiometry as $Rh_2R_2(dmpe)_3$, the dimeric nature of this compound is confirmed by molecular weight studies.

The ^1H n.m.r is simple and comprises of four signals, two sharp singlets at δ + 1.90 and δ + 0.42 due to the alkyl methylene and methyl protons respectively, and two multiplets at δ + 1.25 and δ + 1.05 due to the phosphine methyls and methylenes, (the latter is apparently a quartet.)

The $^{31}P[^1H]$ spectrum is more complicated and is shown in Figure 15 , (the following description uses the labelling scheme used in these figures). The spectrum consists of three discrete sets of signals, two doublets of doublets of doublets (labelled A and M) and at higher field a doublet of doublets of multiplets (X). This can be rationalized in terms of a structure such as



i.e. two square planar Rh(I) centres joined by a bridging phosphine, (the reasons for the labelling scheme will be explained later). Each set of resonances can be treated separately. The doublet of doublets of doublets associated with nucleus A, can be seen to be due to coupling with the rhodium ion ($J_{P_A\text{-}Rh}$ = 150Hz) split again

by the cis phosphorus M, (J_{PA-PM} = 24 Hz) and finally by the trans phosphorus X, (J_{PA-PX} = 376Hz). The magnitude of all these coupling constants is in line with previously reported values for cis and trans two bond phosphorus - phosphorus coupling, and also that between phosphorus and Rh^{I} nuclei.

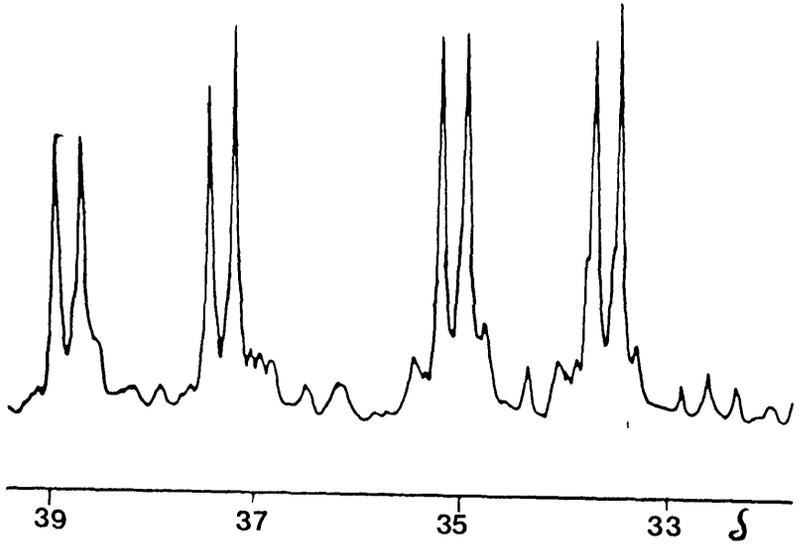
The pattern of signals is qualitatively the same for nucleus M, but here the magnitudes of the coupling constants are smaller, due to coupling with two cis phosphorus nuclei, (J_{PA-PM} = 24Hz, J_{PM-PX} = 35 Hz) and the rhodium nucleus (J_{PM-Rh} = 121Hz). The difference in the magnitude of rhodium-phosphorus coupling constants for P_A and P_M is consistent with the presence of different trans-ligands.

The pattern for the P_X nuclei is much more complicated, three coupling constants are discernable by comparison with those observed in other regions, namely J_{PX-PA} = 376Hz, J_{PX-Rh} = 144Hz, J_{PX-PM} = 34Hz. The other coupling constant arises from the interaction between the phosphorus nuclei at either end of the dmpe bridge, which are magnetically inequivalent. (The simple criterion for this is that the nuclei are not coupled equally to every other nucleus in the spin system). This coupling arises because there is communication between the two phosphorus nuclei either through space or via the carbon backbone. (This is why the nuclei are labelled PX and PX'). This type of coupling has been observed elsewhere (124), and is usually small. Similarly the nuclei designated PA and PA', PM and PM' are magnetically inequivalent, but since there is little or no communication any coupling is negligible.

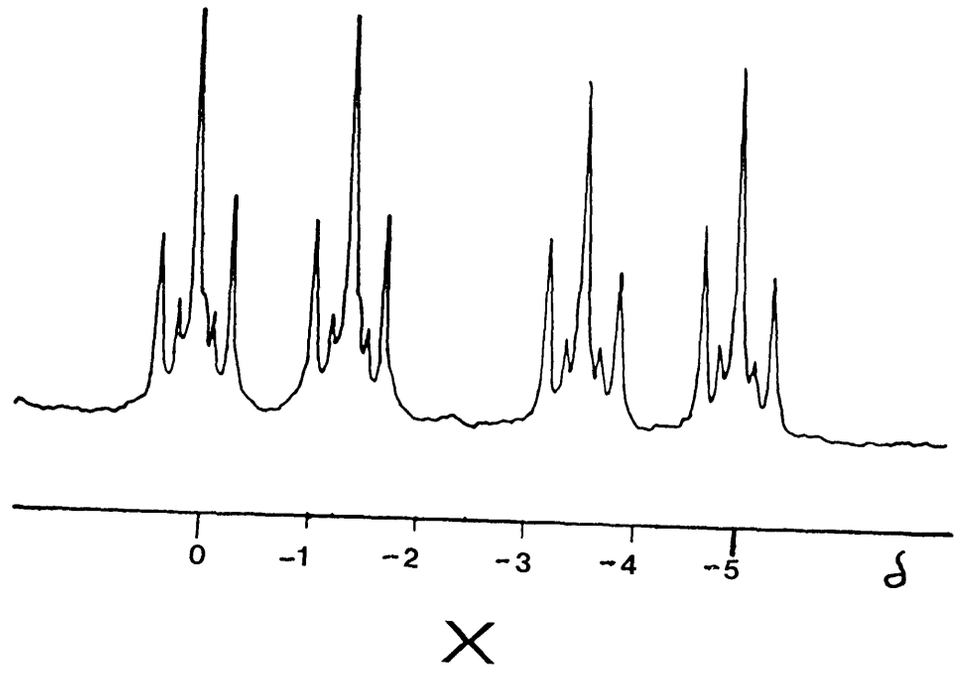
It has not proved possible to determine the magnitude of $\underline{+}J_{PX-PX'}$, this could be obtained using computer simulation, using an AA'MM'XX' spin system, setting $J_{PA-PA'} = \underline{+}J_{PM-PM'} = 0$, and varying $J_{PX-PX'}$ until a good fit between simulated and observed spectra are obtained. Attempts were made to confirm the structure by x-ray crystallographic methods, but suitable crystals could not be obtained.

FIGURE 15

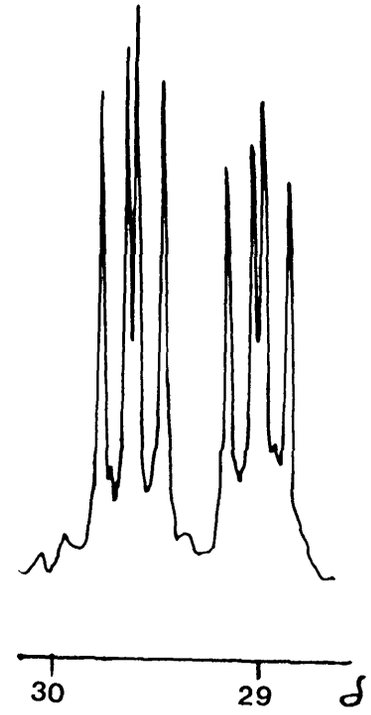
$^{31}P[^{1}H]$ n.m.r. spectrum of $Rh_2(dmpe)_3(CH_2SiMe_3)_2$



A



X



M

TABLE 15 NUCLEAR MAGNETIC RESONANCE DATA FOR RUTHENIUM AND RHODIUM COMPOUNDS

COMPOUND	CHEMICAL SHIFT, δ	
	^{1}H, J (Hz)	^{31}P[^{1}H] J (Hz)
cis $RuMe_2(dmpe)_2$	1·18"t" (8,P-CH_2, "J_{P-H}" = 2.95)	+44.78, t, $^2J_{P-P}$ = 17.72
	1·04 s (24,P-CH_3)	+32.14, t, $^2J_{P-P}$ = 17.73
	0·98 s	
	-0·36 m (6,Ru-Me)	
trans $Ru(CH_2SiMe_3)_2(dmpe)_2$	1·20 m (8, P-CH_2)	+37.30 s
	1·01 (24, P-CH_3)	
	0.92	
	0·37 s (18, -Si-Me_3)	
	-0·60 m	
	-1·40 m (4,Ru-CH_2-)	
cis $Ru(CH_2CMe_2Ph)_2(dmpe)_2$	7·75-7·58 m	+51.93,t,
	7·29-7·08 m (10,-C_6H_5)	$^2J_{P-P}$ = 24.40
		+42.46,t,
		$^2J_{P-P}$ = 24.22
	3.46 m (4,Ru-CH_2)	
	1.33 m (8,P-CH_2)	
	0.84 m (24,P-CH_3)	

	0.94 s	
	0.76 s (12,C-Me)	
Rh Me $(dmpe)_2$ [b]	1.24 m (3, Rh-Me)	+33.70"d"
	0.94 m (8, P-CH_2)	"J_{P-Rh}" = 128
	0.43 m (24,P-CH_3)	
$Rh_2(CH_2SiMe_3)_2(dmpe)_3$ [b]	1.90 s (4,Rh-CH_2)	+36.22"ddd"
		J_{PA-PM} = 24.6
		J_{PA-PX} = 376.0
	1.28 m (36,P-CH_3)	J_{PA-Rh} = 150.4
	1.05 m (12, P-CH_2)	+29.50"ddd"
		J_{PM-PA} = 24.6
		J_{PM-PX} = 35.0
	0.42 s (18, Si-Me_3)	J_{PM-Rh} = 120.8
		-2.36"ddm"
		J_{PX-PM} = 35.2
		J_{PX-PA} = 376.2
		J_{PX-Rh} = 149.4

a) All spectra recorded in C_6D_6

b) refer to text.

TABLE 16 ANALYTICAL DATA FOR RUTHENIUM AND RHODIUM COMPOUNDS

COMPOUND	m.p.,θ/°C	FOUND(REQUIRED) %			
		C	H	P	Si
cis $Ru(Me)_2(dmpe)_2$	237-240d	23.5 (23.4)	9.0 (8.9)	28.9 (28.7)	-
trans $Ru(CH_2SiMe_3)_2(dmpe)_2$	143	41.8 (41.7)	9.4 (9.5)	21.5 (21.5)	
cis $Ru(CH_2CMe_2Ph)_2(dmpe)_2$	143-148d	58.1 (57.6)	8.8 (8.8)	19.1 (18.6)	
Rh $Me(dmpe)_2$ [a]	115	37.3 (37.3)	8.5 (8.4)	29.8 (29.6)	
$Rh_2(CH_2SiMe_3)_2(dmpe)_3$ [b]	185-187	37.9 (37.6)	8.5 (8.5)	22.3 (22.4)	6.7 (6.8)

a) mass spectrum gives parent ion at 417.

b) molecular weight determination (cryoscopically in benzene) gives molecular weight as 850 ($Rh_2R_2(P\text{-}P)_3$ requires 830).

EXPERIMENTAL

All manipulations were carried out in vacuum or under argon. Solvents were distilled under argon from sodium-benzophenone, (hexane, petroleum ether, diethylether, thf, dioxan) sodium (toluene), calcium hydride (dichloromethane) or phosphorus pentoxide (acetonitrile) and degassed prior to use.

Alkylating agents were prepared using literate routes: $Mg(Me)_2$, $Mg(CH_2CMe_3)_2$, $Mg(CH_2SiMe_3)_2$, $Mg(CH_2Ph)_2$ (125) and (126) , as were the tertiary phosphines PMe_3 (127) and dmpe (128) and the platinum metal acetates $Ru(O_2CMe)_4Cl$ (22), $Os_2(O_2CMe)_4Cl_2$ (33c), $Rh_2(O_2CMe)_4$ (129), $([Pd(O_2CMe)_2]_3$ was used as supplied by Johnson Matthey).

Microanalyses were by Pascher, Bonn and Imperial College Microanalytical Laboratories. Melting points were determined in sealed tubes under vacuum.

Spectrometers:-

n.m.r - Jeol FX90Q, Bruker WM 250. Samples prepared in C_6D_6 unless otherwise stated, ^1H referred to Me_4Si, as were $^{13}C[^1H]$. $^{31}P[H]$ referred externally to 85% H_3PO_4 or externally to $P(OMe)_3$ in solvent of choice.

I.r - Perkin Elmer 635, using nujol or voltalef 3S mulls between KBr or CsI plates.

Mass spectrometry - V.G. micromass 7070 and ms-9.

Electrochemistry - Princeton Applied Research EG and G model 174a polagraphic analyser.

Magnetic moment - determined in solution by a modification of the Evans method (97) or in the solid state at ambient temperatures using a J.M.E. magnetic susceptibility balance.

X-ray crystallography - crystals sealed under argon in Lindemann capillaries. All crystallographic measurements were made using a CAD4 diffractometer, operating in W/2θ scan mode with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) in a manner previously described (17).

EXPERIMENTAL - CHAPTER 1

1.1. Hexakis(neopentyl)diruthenium (III)

To a suspension of $Ru_2(O_2CMe)_4Cl$ (1g, 2.1 mmol) in thf (50 cm^3) held at -80°C was added Me_3CCH_2MgCl (36 cm^3 of a 0.35 m solution in diethyl ether, 12.6 mmol). The reaction mixture was allowed to warm slowly to room temperature, giving a crimson solution at about -25°C. After stirring for an additonal twelve hours, the volatile materials were removed under vaccuum, and the residue extracted with hexane (2 x 25 cm^3), giving a purple solution. The combined extracts were filtered and concentrated to ca 20 cm^3, cooling to -20°C overnight yielded purple crystals. Yield 0.32g, 24%.

1.2. Hexakis(trimethylsilylmethyl)diruthenium (III)

To a suspension of $Ru_2(O_2CMe)_4Cl$ (1g, 2.1 mmol) in diethyl ether (50 cm^3) held at -80°C was added Me_3SiCH_2MgCl (17.3 cm^3 of a 0.73m solution in diethyl ether, 12.6 mmol). The reaction was allowed to warm slowly to room temperature, giving an intense blue green solution at about -20°C. After stirring for an additional hour at room temperature, the volatile materials were removed under vacuum. The residue was extracted with hexamethyldisiloxane (2 x 15 cm^3), and the combined extracts filtered and reduced to ca 10 cm^3 cooling at -20°C overnight gave dark green blocks of the title compound. Yield 0.53g, 35%.

An alternative procedure for crystallization involved initial extraction of the reaction residues with hexane, the resulting

green solution was filtered and evaporated to dryness. Extraction of this with diethyl ether, followed by reduction of volume and cooling overnight gave the alkyl in similar yield to that above.

1.3 Tetrakis(neopentyl)bis(μ- acetato)diruthenium (III)

The method of preparation was similar to those above, but using only four equivalents of Me_3CCH_2MgCl, and only stirring for an additional hour after the reaction reached room temperature. (Longer periods lead to the formation of the hexaalkyl in low yield). The product was crystallized from hexane. Yield, 40%.

1.4 Tetrakis(trimethylsilylmethyl)bis(μ-acetato)diruthenium (III)

Again only four equivalents of alkylating agent were used, but here the reaction was evaporated to dryness at 0^oC. The product was again crystallized from hexane,but was considerably more soluble than its neopentyl analogue. Yield 18%.

1.5 Dimethyltetrakis(neopentyl)diruthenium (III)

To a solution of $Ru_2(O_2CMe)_2(CH_2CMe_3)_4$ (0.7g, 1.2 mmol) in hexane (30 cm^3) held at -80^oC was added dimethylmagnesium (2.1 cm^3 of a 0.56 m solution in diethyl ether 1.2 mmols). The reaction was allowed to warm slowly to room temperature, becoming purple at -10^oC. After stirring for one hour at room temperature, the volatile materials were removed under reduced pressure. The residue was extracted with hexane (2 x 20 cm^3), the combined extracts were filtered and reduced to ca 10 cm^3,

cooling to -20°C overnight gave a microcrystalline pink purple product. Yield 0.48g, 78%.

1.6 Diethyl tetrakis(neopentyl)diruthenium) (III)

Prepared in a similar way to the dimethyl but using diethylmagnesium. Crystallization from hexane gave the purple product in 65% yield.

EXPERIMENTAL - CHAPTER 2

2.1 Tetrakis(neopentyl)bis(μ-acetato)diosmium(III)

To a suspension of $Os_2(O_2CMe)_4Cl_2$ (1g, 1.45 mmol) in thf was added $Me_3C\ CH_2MgCl$ (25 cm^3 of a 0.35 m, solution in diethyl ether, 8.75 mmol). The reaction was allowed to warm slowly to room temperature giving a deep red solution at -20°C. After stirring for one hour at room temperature, the volatile materials were removed under reduced pressure and the residue extracted with hexane (2 x 30 cm^3) to give an olive green solution. The combined extracts were filtered and reduced to ca 15 cm^3, cooling at -20°C overnight gave dark green crystals. Yield 0.3g, 28%.

2.2 Tetrakis(trimethylsilyl)bis(μ-acetato)diosmium(III)

This compound was prepared using an identical method but using Me_3SiCH_2MgCl. The compound was isolated as deep red crystals. Yield 24%.

2.3 Tetrakis(neopentyl)bis(η^3allyl)diosmium (III)

To a solution of $Os_2(O_2CMe)_2(CH_2CMe_3)_4$ (0.5g, 0.6 mmol) in hexane (30 cm^3) at -30°C was added allylmagnesiumbromide (3.4 cm^3 of a 0.35m solution in diethyl ether, 1.2 mmol). Sufficient diethyl ether was added to redissolve the Grignard which precipitated initially (ca 10 cm^3). The reaction was allowed to warm slowly to room temperature becoming bright orange at around 0°C. After stirring overnight the volatiles were

removed under vacuum, and the residue extracted with hexane (2 x 20 cm^3). The combined extracts were filtered and reduced to ca 10 cm^3; cooling to -20°C overnight yielded orange crystals. Yield; 0.38g, 85%.

2.4 Tetrakis(cyclohexyl)osmium (IV)

To a suspension of $Os_2(O_2CMe)_4Cl_2$ (1g, 1.45 mmol) in thf (40 cm^3) held at -80°C was added cyclohexylmagnesiumchloride (18.4 cm^3 of a 0.63m solution in diethyl ether, 11.6 mmols) the reaction was allowed to warm slowly to 0°C. It was stirred at this temperature for an additional hour and then the volatile materials were removed under reduced pressure. The residue was extracted with hexane (2 x 25 cm^3) the combined extracts were filtered and reduced to ca 10 cm^3. Cooling to -20°C overnight gave red crystals. Yield 0.18g, 24%.

EXPERIMENTAL - CHAPTER 3

3.1 (2,2 dimethyl-2-silapropane-1,3-diyl)tetrakis(trimethylphosphine)ruthenium (II)

To a solution of $Ru_2(CH_2SiMe_3)_6$ (0.3g, 0.4 mmol) in hexane (40 cm^3) held at -30°C was added PMe_3 (0.5 cm^3, 5 mmol). The colour of the solution changed rapidly from green to red brown. The solution remained unchanged after stirring for an additional twelve hours at room temperature. The solution was filtered and the filtrate reduced in volume to ca 10 cm^3, cooling to -20°C gave brown crystals. Repeated recrystallizations from hexane gave the title compound in 60% yield. (The spectroscopic data for this compound has been reported elsewhere(17a)).

3.2 (2,2 dimethyl-2-silapropane-1,3-diyl)bis(dmpe) ruthenium (II)

As for 3.1, but using a similar excess of dmpe. No reaction was observed at low temperatures, but the solution became red on stirring overnight. After removal of the volatile materials in vacuuo, the residue was extracted with hexamethyldisiloxane (2 x 10 cm^3) and filtered, the combined filtrates were reduced in volume to ca 5 cm^3 and cooled to -20°C overnight. The major product in the form of yellow needles was contaminated with a red oil which was removed by repeated recrystallizations. Yield 36%.

n.m.r : $^1H, \delta(C_6D_6)$ 1.36m, 1.18m, 1.09m (32H, Me-P-CH_2-),
0.54s (6H, $-CH_2-SiMe_2$), 0.14s (4H, $-CH_2-SiMe_2$)
$^{31}P['H]$, $\delta(C_6D_6)$ + 21.08t, J_{P-P} = 15 Hz, + 13.40 t,
J_{P-P} = 14 Hz.

3.3 Hexakis(trimethylsilylmethyl)dioxodiruthenium (V)

Method a.

To a solution of hexakis(trimethylsilylmethyl)diruthenium (III) (0.5g, 0.69 mmol) in hexane (40 cm^3), held at -30°C was added dry oxygen (0.33 cm^3, 0.69 mmol) via syringe. Upon addition the solution immediately changed colour from blue green to deep red. The reaction was allowed to warm to room temperature, filtered to remove black residue and the filtrate evaporated to dryness. The residue was extracted with hexane (1 x 10 cm^3), reduction of volume to ca 5 cm^3 and cooling to -20°C overnight gave deep red blocks. Yield 0.17g, 30%. The removal of all volatile materials after filtering the reaction solution was found to be necessary to remove dissolved oxygen, failure to do this caused decomposition.

Method b.

To a solution of the alkyl (0.5g, 0.69 mmol) in toluene (30 cm^3) held at -78°C was added a solution of nitroso benzene (0.2g, 1.8 mmol) also in toluene (20 cm^3). An immediate colour change to orange-red was discernable. The reaction was allowed to warm to room temperature, and stirred for an additional two hours. The solution was filtered and the volume reduced to ca 15 cm^3, cooling to -20°C overnight gave deep red crystals. Yield 0.63g, 78%, m.p., 112°C d.

Found : C, 37.8; H, 8.7; O, 4.5; Si, 22.0. $Ru_2C_{24}H_{66}O_2Si_6$ requires : C, 38.0; H, 8.7; O, 4.23; Si, 22.2%.

n.m.r : ^1H;$\delta(C_6D_6)$ 1.78,s(12H, $C\underline{H}_2SiMe_3$), 0.46 s (54H,$CH_2Si\underline{Me}_3$)

$^{13}C[^1H]$, $\delta(C_6D_6)$ 35.80 s ($\underline{C}H_2SiMe_3$), 8.43 s ($CH_2Si\underline{Me}_3$)

3.4 Hexakis(neopentyl)dioxodiruthenium (V)

As for 5.1b above using hexakis(neopentyl)diruthenium (III). Reduction of reaction solution volume to ca 25 cm^3 gave red blocks in 45% yield. This compound could not be prepared by the direct interaction of oxygen and the alkyl. m.p., 136°C d.

Found : C, 55.0; H, 9.8; O, 5.3. $Ru_2C_{30}O_2$ requires : C, 54.55; H, 10.0; O, 4.85%.

n.m.r : ^1H, $\delta(C_6D_6)$ 2.94 s (12H,$C\underline{H}_2CMe_3$), 1.24 s (54H,$CH_2C\underline{Me}_3$)
$^{13}C[^1H]$, $\delta(C_6D_6)$ 67.27 s ($\underline{C}H_2CMe_3$), 39.54 s ($CH_2\underline{C}Me_3$), 34.08 s ($CH_2C\underline{Me}_3$)

3.5 Hexakis(trimethylsilylmethyl)bis(n-phenylimido)diruthenium (V)

To a solution of 5.1 (0.1g, 0.13 mmol) in hexane (40 cm^3) held at -30°C was added excess phenyl isocyanate (0.1 cm^3, 1 mmol). The reaction was allowed to warm slowly to room temperature, at -10°C a red brown precipitate formed, which remained after stirring for two hours at room temperature. This was filtered off and extracted with toluene (3 x 20 cm^3). The combined extracts were filtered and reduced to ca 20 cm^3, addition of hexane (5 cm^3) and cooling to -20°C for two days gave a brown microcrystalline product. Yield 0.06g, 56%. Mpt 185-188°C. Found C, 48.0; H, 8.3; N, 3.0. $Ru_2C_{36}H_{76}Si_6N_2$ requires C, 47.7; H, 8.4; N, 3.1%.

n.m.r : ^1H,$\delta(C_7D_8)$ 7.37 m, 7.14 m ($-C_6\underline{H}_5$), 1.62 s (12H,$\underline{CH}_2$-$SiMe_3$)
0.38 s (54H, CH_2-$Si\underline{Me}_3$).

3.6 Hexakis(trimethylsilylmethyl)bis(n-trimethylsilylimido) diruthenium (v)

To a solution of 3.1 (0.3g, 0.39 mmol) in hexane (40 cm^3) was added $Me_3SiN = PMe_3$ (0.2 cm^3, 0.8 mmol). The solution was allowed to stir at room temperature overnight, during which time it became orange. After removal of the volatile materials under vacuum, the residue was washed with hexane (2 x 10 cm^3) and then extracted with toluene (2 x 20 cm^3). The solution was evaporated to dryness and re-extracted with acetonitrile (2 x 10 cm^3), reduction of volume to ca 10 cm^3 and cooling to -20°C for three days gave an orange microcrystalline product (yield 0.13g, 38%). m.p. 198°C,d.

Found : C, 43.0; H, 9.40; N, 3.4. $Ru_2C_{30}H_{84}Si_8N_2$ requires : C, 40.1; H, 9.35; N, 3.1%

n.m.r : ^1H,δ(C_6D_6) 1.58 s (12H, $\underline{CH_2}SiMe_3$), 0.39 s (54H, $CH_2Si\underline{Me_3}$) -0.15 s (18H, $N\text{-}Si\underline{Me_3}$).

$^{13}C['H]$,δ(C_6D_6) 20.32 s ($\underline{CH_2}\text{-}SiMe_3$), 4.58 s ($CH_2\text{-}Si\underline{Me_3}$), -4.8 s ($N\text{-}Si\underline{Me_3}$).

EXPERIMENTAL - CHAPTER 5

Palladium Alkyls

All of the palladium alkyls were prepared by minor modifications of the same general procedure.

5.1 Bis methylbis(trimethylphosphine)palladium (II)

To a suspension of $[Pd(O_2CMe)_2]_3$ (0.3g, 0.45 mmol) in diethyl ether (50 cm^3) was added PMe_3 (1 cm^3, 10 mmol) and dimethylmagnesium (4 cm^3 of a 0.35m solution in diethyl ether, 1.4 mmol) at -78°C. The mixture was allowed to warm slowly to room temperature and stirred for ca twelve hours, after which volatiles were removed in vacuuo. The residue was extracted with hexane (2 x 30 cm^3), the solution filtered reduced to ca 15 cm^3 and cooled to -20°C overnight to give white crystals. Yield 0.3g 75%.

5.2 trans-Bis(trimethylsilylmethyl)bis(trimethylphosphine) palladium (II)

As for above, but using $[Pd(O_2CMe)_2]_3$ (0.37g, 0.55 mmol) in diethyl ether (50 cm^3), PMe_3 (1 cm^3, 10 mmol) and Me_3SiCH_2MgCl (30 cm^3 of a 1.24m solution in diethyl ether 3.7 mmol). Final solution concentrated to ca 5 cm^3. Yield 0.5g, 70%.

5.3 Cis-Bis(neophyl)bis(trimethylphosphine)palladium (II)

As above from $[Pd(O_2CMe)_2]_3$ (0.3g, 0.45 mmol) in diethyl ether (50 cm^3), PMe_3 (1 cm^3, 10 mmol) and Me_2PhCCH_2MgCl (15.5 cm^3 of a 0.09m solution in diethyl ether, 14 mmol). Residue extracted with hexane (3 x 40 cm^3), and subsequently reduced to ca 40 cm^3 before cooling. Yield 0.68g, 72%.

5.4 trans-Bis(benzyl)bis(trimethylphosphine)palladium (II)

As above using $[Pd(O_2CMe)_2]_3$ (0.5g, 0.74 mmol) in toluene (40 cm^3) and bis benzylmagnesium $(PhCH_2)_2Mg$ (6.5 cm^3 of a 0.38m solution in diethyl ether, 2.5 mmol). Final hexane extract reduced to ca 50 cm^3. Yield 0.6g, 60%.

5.5 cis-Bis(trimethylsilylmethyl)(dmpe)palladium (II)

As above using $[Pd(O_2CMe)_2]_3$ (0.5g, 0.74 mmol) in thf (40 cm^3), dmpe (0.33 cm^3, 2.2 mmol) and $(Me_3SiCH_2)_2Mg$ (7.8 cm^3 of a 0.28m solution in diethyl ether 2.2 mmol). Final hexane extract reduced to ca 15 cm^3. Yield 0.65g, 68%.

5.6 cis-Bis(neophyl)(dmpe)palladium (II)

As above using $(Pd[O_2CMe]_2)_3$ (0.5g, 0.74 mmol) in thf (50 cm^3), dmpe (0.33 cm^3, 2.2 mmol) and Me_2PhCCH_2MgCl (25 cm^3 of a 0.09m solution in diethyl ether, 2.3 mmol). Final petroleum extract reduced to ca 20 cm^3. Yield 0.93g, 78%.

5.7 cis-Bis(methyl)(dmpe)palladium (II)

As for 5.6 and 5.5 but using dimethylmagnesium (12.7 cm^3 of a 0.35m solution in diethyl ether, 8.8 mmol). The white product was less soluble, crystallising from ca 40 cm^3 of hexane. Yield 0.49g, 75%.

5.8 cis-Bis(benzyl)(dmpe)palladium (II)

The best yields were obtained by stirring $[Pd(O_2CMe)_2]_3$ (0.5g, 0.74 mmol) and dmpe (0.33 cm^3, 2.2 mmol) in toluene (45 cm^3) at -78°C. To this was added $(PhCH_2)_2Mg$ (6 cm^3 of a 0.38m solution in diethyl ether, 2.3 mmol). After allowing to warm to room temperature the reaction was stirred for two days. After removal of the volatile products the residue was extracted with a mixture of diethyl ether and petroleum (1:10 by volume, 3 x 20 cm^3). Concentration to ca 10 cm^3 and cooling to -10°C overnight yielded yellow crystals. Yields 0.56g, 58%.

5.9 Bis(acetato)bis(trimethylphosphine)palladium (II)

To a solution of the acetate (0.7g, 1.04 mmol) in toluene (70 cm^3) was added excess PMe_3 (1 cm^3, 10 mmol) and the mixture stirred for ca 24 hours. The precipitate was collected and recrystallized from tetrahydrofuran (50 cm^3) as pale yellow crystals. Yield 1.1g, 95%.

5.10 trans-Bis(acetato)bis(dmpe)palladium (II)

As for 9 but using dmpe (2 cm^3, 13.2 mmol). Final recrystallization from tetrahydrofuran gives off white crystals. Yield 0.32g, 56%.

RUTHENIUM ALKYLS

5.11 cis-Bis(methyl)bis(dmpe)ruthenium (II)

To a suspension of $Ru_2(O_2CMe)_4Cl$ (1.0g, 2.1 mmol) in thf (50 cm^3) held at -80°C was added dmpe (1.3 cm^3, 8.4 mmol), after stirring at this temperature for ten minutes dimethylmagnesium (7.5 cm^3 of a 0.56m solution in diethyl ether, 4.2 mmols) was added. The orange-brown reaction mixture was allowed to warm slowly to room temperature, during which time it became a deep red-brown solution. After removal of the volatiles the residue was extracted with hexane (3 x 20 cm^3). The combined extracts were filtered and pumped dry. The complex was purified by vacuum sublimination at 100°C. Yield 1.4g, 78%.

5.12 trans-Bis(trimethylsilylmethyl)bis(dmpe)ruthenium (II)

To a suspension of $Ru_2(O_2CMe)_4Cl$ (1.0g, 2.1 mmol) in thf (50 cm^3) held at -80°C was added dmpe (1.3 cm^3, 8.4 mmol). After stirring for five minutes $(Me_3SiCH_2)_2Mg$ was added (10.7 cm^3 of a 0.78m solution in diethyl ether 8.4 mmols). The red brown reaction mixture was allowed to warm slowly to room temperature, becoming pale orange at -10°C. On stirring for a further 24 hours the colour became yellow. After removal of the volatile

materials under reduced pressure the residue was extracted with hexane (2 x 25 cm^3) to give an orange solution. Reduction of volume to ca 25 cm^3 and cooling to -20°C yielded a brown microcrystalline product. Two further recrystallizations eventually gave a pure product. Yield 0.54g, 42%.

5.13 cis-Bis(neophyl)bis(dmpe)ruthenium (II)

To a suspension of $Ru_2(O_2CMe)_4Cl$ (1.0g, 2.1 mmol) in thf (50 cm^3) held at -80°C was added dmpe (1.3 cm^3, 8.4 mmol) and Me_2PhCCH_2MgCl (14 cm^3 of a 0.6m solution in diethyl ether 8.4 mmol). The brown reaction mixture was allowed to warm slowly to room temperature, after which it was stirred for a further period of twelve hours. The brown solution was evaporated in vacuum and the residue extracted into toluene (3 x 15 cm^3). The bright yellow extract was filtered and reduced to ca 15 cm^3. Cooling to -20°C gave bright yellow crystals. Yield 1.3g, 48%.

RHODIUM ALKYLS

5.14 Methyl bis(dmpe)rhodium (I)

To a suspension of rhodium (II) acetate ($Rh_2(O_2CMe)_4$, 1g, 2 mmol) in thf (50 cm^3) held at -80°C was added dmpe (1.2 cm^3, 8 mmol) and dimethyl magnesium (3.75 cm^3 of a 0.56m solution in diethyl ether, 2.1 mmol). The reaction mixture was allowed to warm slowly to room temperature, becoming a homogeneous yellow solution at -15°C. After stirring for an additional hour at room temperature the volatile materials were removed under reduced pressure and the residue extracted with hexane (4 x 20 cm^3). The

filtered extracts were combined and reduced to dryness, the yellow powder was re-extracted with diethyl ether (2 x 15 cm^3) and filtered. Reduction in volume to ca 10 cm^3 and cooling at -20°C overnight yielded yellow prisms. Yield 0.39g, 45%.

5.15 Bis(trimethylsilylmethyl)tris(dmpe)dirhodium (I)

Method same as for methyl compound above, using rhodium (II) acetate (1g, 2 mmol), dmpe (1.2 cm^3, 8 mmol) and Me_3SiCH_2MgCl (1.7 cm^3 of a 1.3m solution in diethyl ether, 2.1 mmol). On warming to room temperature the reaction mixture became orange red. After removal of the volatile materials, extraction with hexane (2 x 15 cm^3) gave a deep red solution. Reduction of volume to ca 5 cm^3 and cooling to -20°C for three days yielded red crystals. Yield 0.69g, 48%.

REFERENCES

1) L.C. Cadet de Gassicourt, Mem. Math. Phys., 1760, 3, 623.

2) a) E. Frankland, J. Chem. Soc., 1849, 2, 263.

b) E. Frankland, J. Chem. Soc., 1849, 2, 297.

3) E. Frankland, Phil. Trans., 1852, 142, 417.

4) C. Lowig, Annalen, 1853, 88, 318.

5) V. Grignard, C.R. Acad. Sci., 1900, 130, 1322.

6) W.C. Zeise, Ann. Phys., 1827, 9, 632.

7) W.J. Pope and S.J. Peachy, J. Chem. Soc., 1909, 95, 571.

8) F. Hein, Ber., 1919, 52, 195.

9) a) T.J. Kealy, P.L. Pauson, Nature, 1951, 168, 1039.

b) G. Wilkinson, M. Rosenblum, M.C. Whiting and R.B. Woodward, J. Chem. Soc., 1952, 74, 2125.

10) a) G. Wilkinson, Pure Appl. Chem., 1972, 30, 627.

b) W. Mowat, A. Shortland, G. Yagupsky, N.J. Hill, M. Yagupsky and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1972, 533.

11) e.g., G.W. Rice and R.S. Tobias, J. Am. Chem. Soc., 1977, 99, 2141.

12) E. Peligot, Ann. Chim. Phys., 1844, 12, 528.

13) a) F.A. Cotton, B.G. DeBoer, M.D. LaPrade, J.R. Pipal and D.A. Ucko, J. Am. Chem. Soc., 1970, 93, 2926.

b) idem., Acta Crystallogr., B, 1971, 27, 1664.

14) M.C. Chabrie, C.R. Acad. Sci., 1907, 144, 804.

15) J.A. Bertrand, F.A. Cotton and W.A. Dollase, J. Am. Chem. Soc., 1963, 85, 1349.

idem., Inorg. Chem., 1963, 2, 1166.

16) F.A. Cotton, N.F. Curtis, C.B. Harris, B.F.G. Johnson, S.J. Lippard, J.T. Mague, W.R. Robinson and J.S. Wood, Science, 1964, 145, 1305.

17) Ru, Rh, Mo and Cr:-

a) R.A. Andersen, R.A. Jones and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1978, 446.

b) R.A. Andersen, R.A. Jones, G. Wilkinson, M.B. Hursthouse and K.M. Abdul Malik, J. Chem. Soc., Chem. Comm., 1977, 283 and 865.

c) R.A. Jones and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1979, 472.

Os:-

d) T. Behling, G.S. Girolami, G. Wilkinson, R.G. Sommerville and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., 1984, 877.

Pd:- see Chapter 5.

18) F.A. Cotton, J.M. Troup, T.R. Webb, D.H. Williamson and G. Wilkinson, J. Am. Chem. Soc., 1974, 96, 3824.

19) Cr:-

a) F.A. Cotton, S. Koch and M. Millar, Inorg. Chem., 1978, 17, 2014, 2021, 2084 and 2087.

b) idem., J. Am. Chem. Soc., 1977, 99, 7372.

c) idem., Inorg. Chim. Acta, 1977, 25, L105.

Re:-

d) F.A. Cotton, L.D. Gage, K. Mertis, L.W. Shive and G. Wilkinson, J. Am. Chem. Soc., 1976, 98, 6922.

e) R.A. Jones and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1978, 1063; see also 17c.

20) R.A. Jones, Ph.D. Thesis, Univ. of London, 1978.

21) T.A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., 1966, 28, 2285.

22) R.W. Mitchell, A. Spencer and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1973, 846.

23) a) P.S. Braterman and R.J. Cross, Chem. Soc. Rev., 1973, 2, 271.

b) N.A. Dunham and M.C. Baird, J. Chem. Soc., Dalton Trans., 1975, 774.

24) a) F. Huq, W. Mowat, A. Shortland, A.C. Skapski and G. Wilkinson, J. Chem. Soc., Chem. Commun., 1971, 1079.

b) M.H. Chisholm, F.A. Cotton, M. Extine and B.R. Stults, Inorg. Chem., 1976, 15, 2252.

25) a) M.H. Chisholm, F.A. Cotton, B.A. Frenz, W.W. Reichert, L.W. Shive and B.R. Stults, J. Am. Chem. Soc., 1976, 98, 4469.

b) M.H. Chisholm, F.A. Cotton, M. Extine and B.R. Stults, J. Am. Chem. Soc., 1976, 98, 4477.

26) a) M.H. Chisholm, F.A. Cotton, C.A. Murillo and W.W. Reichert, Inorg. Chem., 1977, 16, 1801.

b) A. Akiyama, M.H. Chisholm, F.A. Cotton, M.W. Extine, D.A. Haitko, D. Little and P.E. Fanwick, Inorg. Chem., 1979, 2266.

27) A.R. Chakravarty, F.A. Cotton and D.A. Tocher, J. Am. Chem. Soc., 1985, 106, 6409.

28) L.F. Warren and V.L. Goedken, J. Chem. Soc., Chem. Commun., 1978, 909.

29) K. Nakamoto, "Infra red and Raman Spectroscopy of Inorganic and Coordination Compounds", Wiley, New York, 1978.

30) F.A. Cotton and J.R. Pipal, J. Am. Chem. Soc., 1971, 93, 5541.

31) F.A. Cotton and M.W. Extine, J. Am. Chem. Soc., 1978, 100, 3788.

32) a) M. Rosenblum, Acc. Chem. Res., 1974, 7, 122.

b) G. Carturan, et al, Inorg. Chim. Acta, 1978, 26, 1.

33) a) D.S. Moore, A.S. Alves and G. Wilkinson, J. Chem. Soc., Chem. Comm., 1981, 1164.

b) T.A. Stephenson, D.A. Tocher and M.D. Walkinshaw, J. Organomet. Chem., 1982, 232, C51.

c) T. Behling, G. Wilkinson, T.A. Stephenson, D.A. Tocher and M.D. Walkinshaw, J. Chem. Soc., Dalton Trans., 1983, 2109.

d) A.R. Chakravarty, F.A. Cotton, D.A. Tocher and T.A. Stephenson, Inorg. Chim. Acta, 1984, 87, 115.

34) a) F.A. Cotton and J.L. Thompson, J. Am. Chem. Soc., 1980, 102, 6437.

b) A.R. Chakravarty, F.A. Cotton and D.A. Tocher, Inorg. Chim. Acta, 1984, 89, L15.

35) A.R. Chakravarty, F.A. Cotton and D.A. Tocher, J. Chem. Soc., Chem. Comm., 1984, 501.

36) A.R. Chakravarty, F.A. Cotton and D.A. Tocher, Inorg. Chem., 1984, 23, 4693.

37) P.E. Fanwick, M.K. King, S.M. Tetrick and R.A. Walton, submitted for publication.

38) a) A.N. Nesmeyanov and A.Z. Rubezhov, J. Organomet. Chem., 1978, 164, 259.

b) R.R. Schrock, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., 1974, 951.

39) R.R. Schrock and G.W. Parshall, Chem. Rev., 1976, 76, 243.

40) a) K.H. Thiele, R. Opitz and E. Kohler, Z. Anorg. Allg. Chem., 1977, 435, 45.

b) W. Seidel and I. Burger, J. Organomet. Chem., 1979, 171, C45; ibid., 1979, 177, C19.

c) R. Kirmse and W. Seidel, Z. Anorg. Allg. Chem., 1982, 490, 19.

d) C. Cauletti, R. Zanoni and W. Seidel, Z. Anorg. Allg. Chem., 1983, 495, 143.

41) a) K. H. Thiele, A. Russek, R. Opitz, B. Mohai and W. Bruser, Z. Anorg. Allg. Chem., 1975, 412, 11.

b) L. Bencze, K.H. Thiele and V. Marquardt, Recl. Trav. Chim. Pays-Bas, 1977, 96, M8.

c) R. Opitz, L. Bencze, L. Marco and K.H. Thiele, J. Organomet. Chem., 1974, 71, C3.

42) a) G.R. Davies, J.A.J. Jarvis and B.T. Killbourne, J. Chem. Soc., Chem. Commun., 1971, 1511.

b) I.W. Bassi, G. Allegra, R. Scordamaglia and G. Chioccola, J. Am. Chem. Soc., 1971, 93, 3787.

43) G.R. Davies, J.A.J. Jarvis, B.T. Killbourne and A.J.P. Pioli, J. Chem. Soc., Chem. Comm., 1971, 677.

44) T. Glowiak, R. Grobelny, B. Jezowska-Trzebiatowska, G. Kreisel, W. Seidel and E. Uhlig, J. Organomet. Chem., 1978, 155, 39.

45) V. Gramlich and K. Pfefferkorn, J. Organomet. Chem., 1973, 61, 247.

46) C.J. Cardin, D.J. Cardin, J.M. Kelly, R.J. Norton, A. Roy, B.J. Hathaway and T.J. King, J. Chem. Soc., Dalton Trans., 1983, 671.

47) R.P. Tooze, P. Stavropoulos, M. Motevalli, M.B. Hursthouse and G. Wilkinson, J. Chem. Soc., Chem. Commun., 1985, 1139.

48) W. Seidel and I. Burger, Z. Chem., 1977, 17, 185.

49) W. Seidel and I. Burger, Z. Anorg. Allg. Chem., 1976, 426, 155.

50) F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 4th edition, Wiley-Interscience, New York, N.Y., 1980, p. 1138.

51) P.R. Sharp, D. Astruc and R.R. Schrock, J. Organomet. Chem., 1979, 182, 477.

52) G.S. Girolami, C.G. Howard, G. Wilkinson, H.M. Dawes, M. Thornton-Pett, M. Motevalli and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., 1985, 921 and references therein.

53) J.B. Weber, J. Porret and A. Jacot-Guillarmod, Helv. Chim. Acta, 1978, 61, 2949.

54) a) "Reactivity of Metal-Metal Bonds", ed. M.H. Chisholm, ACS Symp. Ser., 1981, 155, 17.

b) M.H. Chisholm, D.M. Hoffman and J.C. Huffman, Chem. Soc. Rev., 1985, 14, 69.

55) M.H. Chisholm, F.A. Cotton, M.W. Extine and W.W. Reichert, J. Am. Chem. Soc., 1978, 100, 153.

56) R.E. Myers, Ph.D. Thesis, Purdue University, 1977.

57) a) S.D. Chappell and D.J. Cole-Hamilton, Polyhedron, 1982, 1, 739.

b) I.P. Rothwell, Polyhedron, 1985, 4, 177.

58) T.H. Tulip and D.L. Thorn, J. Am. Chem. Soc., 1981, 103, 2448.

59) K.I. Gell and J. Schwartz, J. Am. Chem. Soc., 1981, 103, 2687.

60) A.J. Lindsay, private communication.

61) I.R. Beattie and P.J. Jones, Inorg. Chem., 1979, 18, 2318.

62) a) Y. Iwasawa, M. Yamagishi and S. Ogasawara, J. Chem. Soc., Chem. Comm., 1980, 871.

b) Y.E. Yermakov, Catal. Rev. Sci. Eng., 1976, 13, 77.

c) D.G.H. Ballard, Adv. Catal., 1973, L3, 263.

d) Y. Iwasawa and H.J. Hamamura, J. Chem. Soc., Chem. Commun., 1983, 130.

63) W.A. Hermann, R. Serrano and H. Bock, Ang. Chem. Int. Edn., 1984, 23, 383.

64) J.H. Holloway and R.D. Peacock, J. Chem. Soc., 1963, 527.

65) E.A. Seddon and K.R. Seddon "The Chemistry of Ruthenium", Elsevier, Amsterdam, 1984, chapter 6.

66) M.H. Chisholm "Reactivity of Metal-Metal bonds", A.C.S. Symposium Series, 1981.

67) R. Eisenberg, A.P. Gaughan Jr., C.G. Pierpont, J. Reed and A.J. Shultz, J. Am. Chem. Soc., 1972, 94, 6240.

68) "Metal Ion Activation of Dioxygen", T.G. Spiro, Wiley, New York, 1980.

69) a) W.P. Griffith, Coord. Chem. Rev., 1970, 5, 549.

b) D.J. Gulliver and W. Levason, Coord. Chem. Rev., 1982, 46, 1.

70) N.M. Boag and H.D. Kaesz in "Comprehensive Organometallic Chemistry", eds. G. Wilkinson, F.G.A. Stone and E.W. Abel, Vol. 4, Chapter 30.6, 1982.

71) a) P.N. Dwyer, L. Puppe, J.W. Buchler and W.R. Scheidt, Inorg. Chem., 1975, 14, 1782.

b) R. Guilard, Inorg. Chem., 1978, 17, 1228.

72) a) H. Alper and J.F. Petrignani, Inorg. Chim. Acta, 1983, 77, L243.

b) H. Alper, J.F. Petrignani, F.W.B. Einstein and A.C. Willis, J. Am. Chem. Soc., 1983, 105, 1701.

73) K.F. Mertis, A.F. Masters and G. Wilkinson, J. Chem. Soc., Chem. Comm., 1978, 858.

74) W.A. Hermann, R. Serrano, V. Kusthardt, M.L. Ziegler, E. Goggolz and T. Kahn, Ang. Chem. Int. Edn., 1984, 23, 515.

75) W.P. Griffith and D. Pawson, J. Chem. Soc., Dalton Trans., 1973, 1315.

76) a) C.M. Che, K.Y. Wong and T.C.W. Mak, J. Chem. Soc., Chem. Commun., 1985, 546.

b) C.M. Che, K.Y. Wong and C.K. Poon, Inorg. Chem., in press.

77) T.C. Mak, C.M. Che and K.Y. Wong, J. Chem. Soc., Chem. Commun., 1985, 986.

78) R.A. Sheldon and J.A. Van Doorn, J. Organomet. Chem., 1975, 94, 115 and references therein.

79) a) H. Minoun, M.M. Perez Machirant and I. Seree de Roch, J. Am. Chem. Soc., 1978, 100, 5437.

b) H. Mimoun, J. Mol. Catal., 1980, 7, 1.

80) R.A. Sheldon and J.K. Kochi, Adv. Catal., 1976, 25, 272.

81) R. Landau, G.A. Sullivan and D. Brown, Chemtech, 1979, 9, 602.

82) M.A. Andrews, T.C. Chang, Chi-wen Cheng and K.P. Kelly, Organometallics, 1984, 3, 1777.

83) K.B. Sharpless, A.Y. Teranishi and J.E. Backwall, J. Am. Chem. Soc., 1977, 99, 3120.

84) a) J.L. Herisson and Y. Chauvin, Makromol. Chem., 1970, 141, 161.

b) R.H. Grubbs, Prog. Inorg. Chem., 1978, 24, 1.

85) A.C. Dengel, R.A. Hudson, W.P. Griffith, Transition Met. Chem., 1985, 10, 98.

86) a) D.C. Bradley, M.B. Hursthouse, K.M. Abdul Malik, A.J. Neilson and R.L. Short, J. Chem. Soc., Dalton Trans., 1983, 2651.

b) E.A. Maata, Inorg. Chem., 1984, 23, 2560.

87) A.O. Chong, K. Oshima, K.B. Sharpless, J. Am. Chem. Soc., 1977, 79, 3420.

88) M.H. Chisholm, F.A. Cotton, M.W. Extine and R.L. Kelly, J. Am. Chem. Soc., 1979, 101, 7645.

89) F.A. Cotton and R.A. Walton, "Multiple bonds between metal atoms", Wiley-Interscience, New York, 1982.

90) J.G. Norman Jr., G.E. Renzoni and P.A. Case, J. Am. Chem. Soc., 1979, 101, 5256.

91) a) F.A. Cotton and E. Petersen, Inorg. Chem., 1975, 14, 383.

b) C.R. Wilson and H. Taube, Inorg. Chem., 1975, 14, 2276, see also reference 22.

92) a) T. Malinski, D. Chang, F.N. Feldmann, J.L. Bear and K.M. Kadish, Inorg. Chem., 1983, 22, 3225.

b) M.Y. Chavan, F.N. Feldmann, X.Q. Lin, J.L. Bear and K.M. Kadish, Inorg. Chem., 1984, 23, 2373, see also reference 27.

93) a) D. Rose and G. Wilkinson, J. Chem. Soc., 1970, 1791.

b) J.D. Gilbert, D. Rose and G. Wilkinson, J. Chem. Soc., 1970, 2765.

94) A.J. Lindsay, G. Wilkinson, M. Motevalli and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., accepted for publication.

95) M. Berry, C.D. Garner, I.H. Hillier, A.A. MacDonald and W. Clegg, Inorg. Chim. Acta, 1981, 53, L61.

96) A. Bino, F.A. Cotton and T.R. Felthouse, Inorg. Chem., 1979, 18, 259.

97) D.F. Evans, G.V. Fazakerly and R.F. Phillips, J.C.S. (A), 1971, 1931.

98) G.G. Stanley, Ph.D. Thesis, Texas A and M University, 1979.

99) J.G. Norman Jr., and H.J. Kolari, J. Am. Chem. Soc., 1978, 100, 791.

100) J.G. Norman Jr., H.J. Kolari, H.B. Gray and W.C. Trogler, Inorg. Chem., 1977, 16, 987.

101) T.J. Goodwin and G. Wilkinson, unpublished results.

102) S.A. Fouda and G. Rempel, Inorg. Chem., 1979, 18, 1.

103) P. Legzdins, R.W. Mitchell, G.L. Rempel, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. (A), 1970, 3322.

104) B.C.Y. Hui, W.K. Teo and G.L. Rempel, Inorg. Chem., 1973, 12, 758.

105) J.A. Osborne, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. (A), 1966, 1711.

106) a) T. Ito, H. Tsuchiya and A. Yamamoto, Bull. Chem. Soc. Jap., 1977, 50, 1319.

b) J. Chatt and B. Shaw, J. Chem. Soc., 1962, 5075.

107) R. Uson, J. Fornies, F. Martinez and J. Tomas, J. Chem. Soc., Dalton Trans., 1980, 888.

108) I.I. Moiseev and M.N. Vargaftik, Dokl. Akad. Nauk, SSSR, (English translation) 1966, 166, 81.

109) R.F. Heck, J. Organomet. Chem., 1972, 37, 389.

110) G. Calvin and G.E. Coates, Chem. Ind. (London), 1958, 160.

111) T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer and G. Wilkinson, J. Chem. Soc., 1965, 3632.

112) G.E. Coates and C. Parkin, J. Chem. Soc., 1963, 421.

113) H. Werner and W. Bertloff, J. Chem. Res. (S), 1978, 201.

114) B. Wozniak, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. (A), 1971, 3116.

115) P.M. Maitlis, P. Espinet and M.J.H. Russel in "Comprehensive Organometallic Chemistry", eds. G. Wilkinson, F.G.A. Stone and E.W. Abel, Vol. 6, Chapter 38.4, 1982.

116) a) D.T. Rosevear and F.G.A. Stone, J. Chem. Soc. (A), 1968, 164.

b) P. Diversi, G. Ingrosso and A. Lucherni, J. Chem. Soc., Chem. Commun., 1978, 735.

c) P. Diversi, D. Fasce and R. Santini, J. Organomet. Chem., 1984, 269, 285.

d) R. Uson, J. Fornies, J. Gimeno, P. Espinet and R. Navaro, J. Organomet. Chem., 1974, 81, 115.

e) G. Calvin and G.E. Coates, J. Chem. Soc., 1960, 2008.

117) J. Chatt, F.A. Hart and H.R. Watson, J. Chem. Soc., 1962, 2537.

118) E.O. Greaves, R. Bruce and P.M. Maitlis, J. Chem. Soc., Chem. Commun., 1967, 860.

119) S. Ahrland, J. Chatt and N.R. Davies, Quart. Rev. Chem. Soc., 1958, 12, 265.

120) C.M. Harris, R.S. Nyholm and N.C. Stephenson, Nature, 1956, 177, 1127.

121) R.A. Porter and D.F. Shriver, J. Organomet. Chem., 1975, 90, 41.

122) J. Chatt and R.G. Hayter, J. Chem. Soc. (A), 1963, 6017.

123) P.S. Pregosin and R.W. Kunz, "^{31}P and ^{13}C n.m.r. of Transition Metal Phosphine Complexes", Springer Verlag, Berlin/New York, 1979, Vol. 16.

124) A.T. Hutton, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., 1985, 1677.

125) A. Jacot-Guillarmod, R. Tabacchi and J. Parret, Helv. Chim. Acta, 1970, 53, 1491.

126) R.A. Andersen and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1977, 809.

127) W. Wolfsberger and H. Schmidbaur, Synth. React. Inorg. Metal-Org. Chem., 1974, 4, 149.

128) R.J. Burt, J. Chatt, W. Hussain and G.J. Leigh, J. Organomet. Chem., 1979, 182, 203.

129) G.A. Rempel, P. Legzdins, H. Smith and G. Wilkinson, Inorg. Synth., 1972, 33, 3479.