ORGANOMETALLIC COMPOUNDS OF RHENIUM AND THE PLATINUM GROUP METALS

A thesis submitted by

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ABSTRACT

The interaction of Grignard reagents with $Ru_2(O_2CMe)_4$, $Ru_2(O_2CMe)_4Cl$, $(Et_4N)[RuCl_5(thf)]$ and $(^nPr_4N)[RuO_4]$ leads to the diamagnetic ruthenium(IV) complexes, RuR_4, where R=c-C_6H_{11}, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$ and 4-^{t}BuC_6H_4. X-ray crystallography of the cyclohexyl and 2-methylphenyl complexes show tetrahedral geometry.

The reaction of $ReCl_4(thf)_2$ with 2-methylphenylmagnesium bromide leads to the isolation of tetrakis(2-methylphenyl)rhenium(IV), and air oxidation of this compound allows the isolation of the paramagnetic oxotetrakis(2-methylphenyl)rhenium(VI) compound; both compounds have been characterised by X-ray crystallography. Further reactions of $Re(2\text{-}MeC_6H_4)_4$ with NO, Cl_2, tempo and $AgBF_4$ have been studied. The interaction of xylylmagnesium bromide with $(Me_3NH)[ReO_4]$ or Re_2O_7 leads to the isolation of the diamagnetic rhenium(V) complex $[(xylyl)_2ReO_2]_2Mg(thf)_2$, which can be oxidised to the paramagnetic $ReO_2(xylyl)_2$ compound, the X-ray crystal structure of which revealed tetrahedral geometry. An improved high yield synthesis of ReO_2R_2 (R=xylyl or mesityl) is also reported from the reaction of $O_3Re(OSiMe_3)$ with the appropriate Grignard. The interaction of $O_3Re(OSiMe_3)$ with $Al(mesityl)_3thf$ yields the diamagnetic $O_3Re(mesityl)$ complex.

The interaction of 4-^{t}butylphenylmagnesium bromide with OsO_4 leads to the isolation of $Os(4\text{-}^tBuC_6H_4)_4$. Reaction of OsO_4 with xylyl Grignard yields the air stable $OsO_2(xylyl)_2$ compound, whose structure has been determined by X-ray crystallography. Friedel-Crafts acylation of $Os(2\text{-}MeC_6H_4)_4$ has also been investigated to yield the partially acylated compound $Os(2\text{-}MeC_6H_4)_3(2\text{-}Me\text{-}4\text{-}COMeC_6H_3)$.

The complex $Re(CSiMe_3)(CH_2SiMe_3)_3Cl$ has been isolated from the reaction of $ReCl_4(thf)_2$ with Me_3SiCH_2MgCl and the complex has been characterised by X-ray crystallography to reveal trigonal bipyramidal geometry.

The interaction of cycloalkyl Grignards with $CrCl_3(thf)_3$ yields the paramagnetic $Cr(cycloalkyl)_4$ compounds. The X-ray structure of $Cr(C\text{-}C_6H_{11})_4$ has been determined to show tetrahedral geometry.

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LIST OF ABBREVIATIONS

Å	angstrom unit, 10^{-8} cm.
atm	101 325 Nm^{2}.
B.M.	Bohr Magnetons ($0.927 \times 10^{-23} Am^{2}$).
b.p.	boiling point.
t_{Bu}	*tert*-butyl CMe_3.
c	cyclo.
°C	degrees Celsius.
cm^{-1}	wave number.
δ	delta, chemical shift.
E.S.R.	electron spin resonance.
Et	ethyl CH_2CH_3.
eV	electron volt.
g	gram.
g	*g*-values.
h.	hour.
Hz	hertz, sec^{-1}.
i.r.	infrared.
J	coupling constant.
K	kelvin.
Me	methyl, CH_3.
μ_{eff}	effective magnetic moment.
mesityl	2,4,6-trimethylphenyl.
m.p.	melting point.
mT	millitesla,10 gauss.
n.m.r.	nuclear magnetic resonance.
PMe_3	trimethylphosphine.
Ph	phenyl, C_6H_5.

p.p.m.	parts per million.
Pr	propyl, $CH_2CH_2CH_3$.
py	pyridine, C_5H_5N.
R	alkyl or aryl group.
o-tolyl	2-methylphenyl.
thf	tetrahydrofuran.
u.v.	ultra violet.
X	halogen.
xylyl	2,6-dimethylphenyl.
ν	frequency in cm^{-1}.

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ONWARDS AND UPWARDS

Dedicated to Peter, Brenda, Gary
and all the family

INTRODUCTION

In the past thirty years the interest in the field of organotransition metal chemistry has increased rapidly. This is a result of early observations that organotransition metal compounds not only possessed many new and unusual properties, but also that some were capable of promoting novel, specific and occasionally significant processes. These factors have prompted more and more scientists, some from widely different disciplines, to study organotransition metal compounds in a continuing effort to elucidate the fundamental principles associated with the chemistry of these compounds, and in some cases, to emulate the efficiency and selectivity of natural biometallic processes.

Although organometallic chemistry is considered to be a hybrid between the classical subdivisions of inorganic and organic chemistry, the rapidly advancing subject has clearly contributed to and benefitted from advances in both. Many consider the subject to be much younger than the other two branches, although the first organometallic compound, tetramethyldiarsine was synthesised as long ago as 1760 by Cadet de Gassicourt [1] and the first recognised organometallic complex, Zeise's salt, $K[PtCl_3(C_2H_4)]$ [2] was prepared in 1827.

However, the significance of these isolated results was not realised at the time and the subject's true beginnings can be attributed to Frankland in 1849 [3] with the isolation of zinc alkyls. It was work by Grignard [4] on magnesium alkyls, and the isolation of other such compounds *e.g.* for mercury [5], tin [5] and lead [6] that, with the discovery of zinc alkyls, laid the foundation for modern organometallic chemistry.

The emergence of compounds containing bonds between transition

metals and carbon came more recently, although once again isolated compounds precede the real beginning, *e.g.* trimethylplatinum iodide [7] by Pope and Peachy in 1909 and the ill-characterised polyphenylchromium made by Hein in 1919 [8].

The isolation and structure determination of ferrocene [9] in 1952 marked the birth of a new era in organotransition metal chemistry. It was subsequently realised that the transition metals possessed the capability to form a wide range of isolable organometallic compounds. Most earlier attempts to prepare these compounds had failed because the stabilities of the compounds are very dependent on the particular groups attached to the metal and stable combinations were not found.

This failure generated a serious misconception that hampered development in the field, namely that transition metal to carbon bonds are weak and because of this such compounds are intrinsically thermodynamically unstable, only being isolated in the presence of stabilising ancillary ligands. It was eventually realised [10] that it was kinetic instability that led to decomposition, which could be prevented by careful choice of alkyl group, metal oxidation state, other ligands or coordination number and geometry.

Organometallic transition metal alkyl or aryl compounds are now known for most transition metals, and homoleptic neutral compounds are known for Ti, V, Cr, Mn, Fe, Co and Ni for the first row elements, Zr, Nb, Mo and Ru for the second row, and Hf, Ta, W, Re and Os for the third row. These compounds have the formulae, MR_n (n = 2,3,4,5 and 6), M_2R_6 and M_3R_{12}, and are mentioned in a number of invaluable general reference works [11-14], except for Ru, Os and Re (see Chapters 1, 3 and 2 respectively and references therein).

The work described in this thesis concerns the synthesis, characterisation and reaction chemistry of homoleptic alkyls and aryls of groups VI, VII and VIII. Noticeably the heavier elements, Ru, Os and Re have been used in synthesising novel homoleptic compounds in high oxidation states as well as some oxo-aryl compounds of Os and Re. At the beginning of each chapter I have presented a small review of the relevant homoleptic alkyl/aryl and oxo-aryl chemistry for that particular topic.

CHAPTER 1

HOMOLEPTIC ALKYL AND ARYL COMPOUNDS OF RUTHENIUM

HOMOLEPTIC ALKYL AND ARYL COMPOUNDS OF RUTHENIUM

Introduction

Until 1984, no homoleptic alkyls or aryls of the platinum group metals were known. While unstable alkylate anions of palladium and platinum such as $[PtMe_6]^{2-}$ exist[15], more stable perchlorinated aryl anions of Pt^{II} and Pt^{III}, $[Pt(C_6Cl_5)_4]^{-1,-2}$, have been characterised and shown by X-ray to have square planar geometries[16].

More recent work by Wilkinson and Tooze[17] has established a new type of homoleptic ruthenium alkyl, $Ru_2(alkyl)_6$. The mixed alkyl, $Os_2(\eta^3\text{-}C_3H_5)_2(CH_2CMe_3)_4$ has also been isolated from the partially alkylated compound $Os_2(\mu\text{-}O_2CMe)_2(CH_2CMe_3)_4$[17]. Homoleptic osmium (IV) tetraalkyls and tetraaryls, namely $Os(cyclohexyl)_4$, $Os(2\text{-}MeC_6H_4)_4$ and $Os(phenyl)_4$[18] have also been made (see C.3 for further discussion).

Although oxo-alkyl and oxo-aryl compounds are known for both rhenium[19] and osmium[19,20], only two oxo-alkyls of ruthenium have ever been isolated. The reaction of the dimeric hexaalkyls with either dioxygen or nitrosobenzene at -80°C gives $Ru_2O_2R_6$, where R = CH_2SiMe_3 or CH_2CMe_3[17].

In this chapter, further investigation on various ruthenium starting materials, $Ru_2(O_2CMe)_4Cl$, $Ru_2(O_2CMe)_4$, $(Et_4N)[RuCl_5(thf)]$, $(Et_4N)[RuCl_5(MeCN)]$ and $(^nPr_4N)[RuO_4]$ has yielded the first homoleptic tetraalkyl and tetraaryl ruthenium(IV) compounds[18b, 21].

Results and Discussion

(A)(i) Tetrakis(cyclohexyl)Ruthenium(IV)

The first momomeric homoleptic alkyl of the platinum metals to be isolated was $Os(C\text{-}C_6H_{11})_4$ [18]. Strangely, the cyclohexyl ligand has only rarely been used in the synthesis of transition metal tetraalkyl compounds, and the only other stable compounds, $Cr(C\text{-}C_6H_{11})_4$ and $Ru(C\text{-}C_6H_{11})_4$ are reported in this thesis. The analogous titanium compound, $Ti(C\text{-}C_6H_{11})_4$ decomposes above -30°C [22]. Although a considerable number of metal tetraalkyl compounds have been isolated for several of the early transition metals, Ti, Zr, Hf, V and Cr [13], none were known for the platinum group metals.

The reaction of excess cyclohexylmagnesium chloride with the dimeric acetate chloride, $Ru_2(\mu\text{-}O_2CMe)_4Cl$, gives the tetrakis-(cyclohexyl)ruthenium(IV) compound in moderate yield. Less bulky alkylating agents (*e.g.* CH_2SiMe_3 and CH_2CMe_3) give different products [17] with the acetate chloride. The reaction is clearly complicated, probably involving disproportionation:

$$Ru_2^{II,III} \longrightarrow Ru^{IV} + Ru^{I}$$

but no other metal compounds could be isolated.

However, attempts to synthesise tetraalkyls of ruthenium from other starting materials (*e.g.* $(Et_4N)[RuCl_5(thf)]$ and $(^nPr_4N)[RuO_4]$) with methyl, trimethylsilylmethyl, neopentyl, cyclopentyl and benzyl Grignard reagents all resulted in decomposition after initial deep red colouration at -78°C. Even in the presence of co-ordinating ligands such as pyridine and trimethylphosphine, no products could be characterised.

It is interesting to note that tetrakis(cyclohexyl)ruthenium(IV) cannot be prepared from $(Et_4N)[RuCl_5(thf)]$.

The i.r. spectrum of $Ru(C\text{-}C_6H_{11})_4$ shows the expected cyclohexyl ligand vibrations. The ^1H n.m.r. spectrum is complex, comprising two multiplets centred at δ 2.62 (1H, due to the α-hydrogen) and δ 1.58 (10H); the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum consists of four sharp singlets at δ 49.7, 33.5, 27.5 and 27.7, for the four unique carbon atoms. The mass spectrum shows the parent ion ^{102}Ru(32% abundance) m/e 434 (80%) $Ru(C\text{-}C_6H_{11})_4^+$, and peaks for the other ruthenium isotopes (*e.g.* ^{101}Ru(13% Ab.) m/e 433 (47%) and peaks for ^{96}Ru, ^{99}Ru, ^{100}Ru and ^{104}Ru). Peaks for the $Ru(C\text{-}C_6H_{11})^+$, m/e 184 (25%) and the cyclohexyl ligand m/e 83 (13%) are also present. The ruthenium compound is readily soluble in ethers, aliphatic and aromatic solvents, but it is air-sensitive both in the solid state and in solution. This molecule was the first tetrahedral organometallic ruthenium(IV) compound to be isolated.

The molecular structure of the ruthenium compound [18b] is shown in Figure 1.1; selected bond lengths and angles are collected in Table 1.1. The molecule is sited on a crystallographic two-fold axis, and the effective symmetry approaches $\bar{4}$. Thus the two independent Ru-C bond lengths are equal within the limits of error, the twists of the two independent rings [*i.e.* representative torsion angles about the Ru-C bonds, *e.g.* C(n1')-Ru-C(n1)-C(n2)(n=1 or 2)] differ by only 1 or 2°, and the dihedral angles between the C(11')-Ru-C(11), C(21')-Ru-C(21) planes is 91.1°. As with $Os(C\text{-}C_6H_{11})_4$ [18b] the RuC_4 tetrahedra are slightly flattened in the direction of the two-fold axis, with C(11, 11')-Ru-C(21,21') 116-116.2° and C(11,11')-Ru-C(21,21') 105.4-107.1°. The cyclohexyl rings all lie approximately

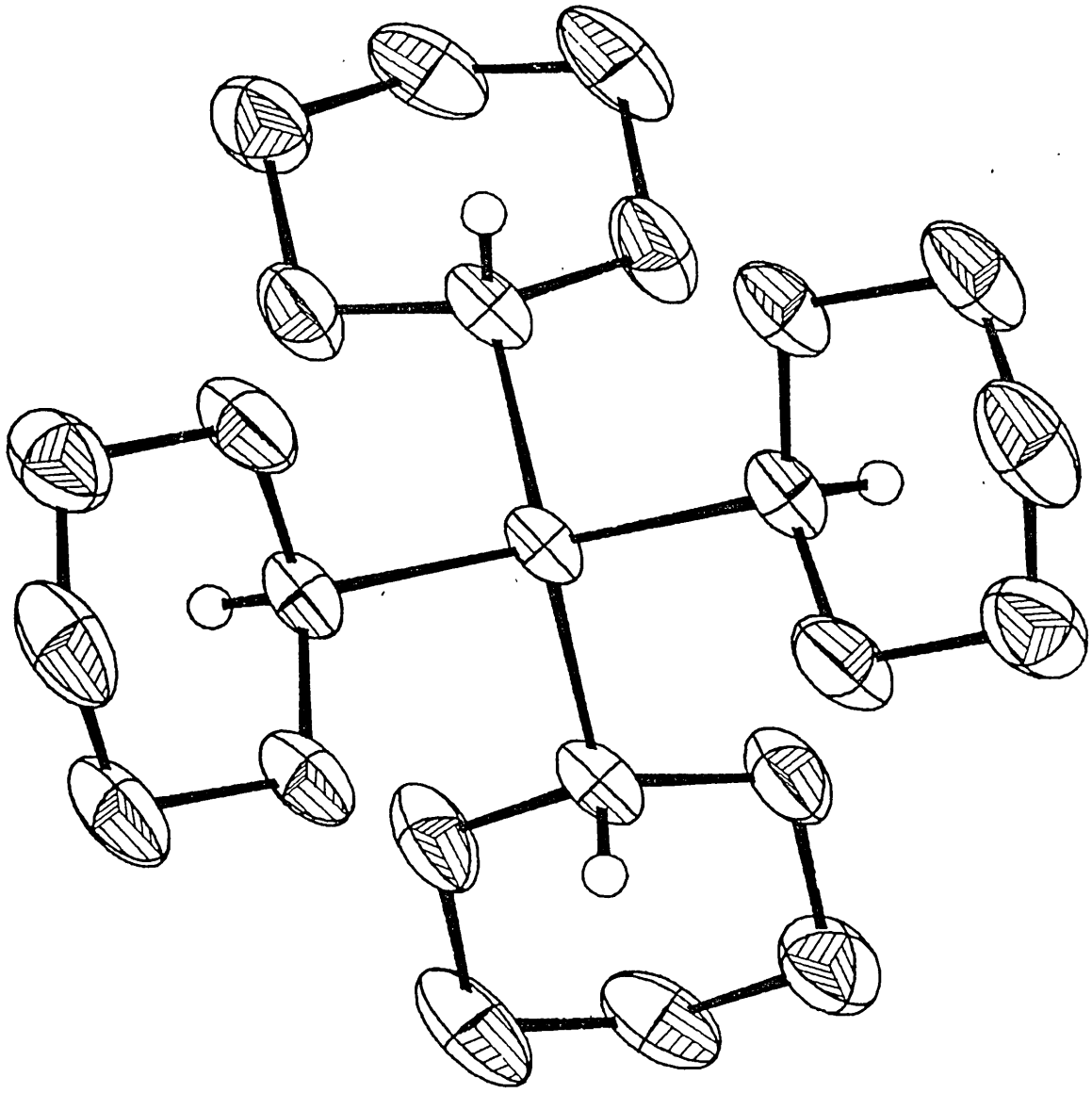


Figure 1.1: The molecular structure of $Ru(C\text{-}C_6H_{11})_4$.

Table 1.1: Bond lengths and angles for $Ru(C\text{-}C_6H_{11})_4$.

Bond Lengths (Å) for $Ru(C\text{-}C_6H_{11})_4$

Ru-C(11)	2.020
Ru-C(21)	2.018
C(11)-C(12)	1.519
C(11)-C(16)	1.515
C(21)-C(22)	1.521
C(21)-C(26)	1.526

Bond Angles (deg.) for $Ru(C\text{-}C_6H_{11})_4$

C(11)-Ru-C(11')	116.2(3)
C(21)-Ru-C(21')	116.0(3)
C(11)-Ru-C(21)	107.1(2)
C(11')-Ru-C(21)	105.4(2)
Ru-C(11)-C(12)	114.4(3)
Ru-C(11)-C(16)	112.4(3)
Ru-C(21)-C(22)	114.3(3)
Ru-C(21)-C(26)	113.0(3)
C(12)-C(11)-C(16)	111.0(4)
C(22)-C(21)-C(26)	110.8(4)

in chair formations. No interactions between the metal centre and the α-hydrogens are discernable. These hydrogens were located in the X-ray diffraction study and are included in the molecular structure. This tetrahedral structure is in agreement with the observed diamagnetism of the compound, and is consistent with an e^4 (low spin) electronic configuration.

(B) Tetraaryls of Ruthenium(IV)

The interaction of aryl Grignards with tetraethylammonium pentachloro(solvent)ruthenate(IV), (solvent = acetonitrile or tetrahydrofuran), yields homoleptic, tetrahedral ruthenium(IV) species, $Ru(aryl)_4$, where aryl = 2-methylphenyl, 2,6-dimethylphenyl and 4-^{t}butylphenyl. Tetrakis(mesityl)ruthenium(IV), mesityl = 2,4,6-trimethylphenyl, and tetrakis(2-methylphenyl)ruthenium(IV) can be obtained from the reaction of diruthenium(II,II)tetraacetate, $Ru_2(\mu\text{-}O_2CMe)_4$, with the appropriate Grignard reagents. It should be noted that no product could be isolated from the reaction of $(Et_4N)[RuCl_5(thf)]$ with phenyllithium or phenylmagnesium bromide, even in the presence of pyridine. Presumably, the ruthenium nucleus is insufficiently shielded to prevent *ortho*-hydrogen abstraction from occurring [13], leading to decomposition, although one cannot rule out other electronic and steric effects.

The reaction of $(^n Pr_4N)[RuO_4]$ with four equivalents of $Al(Ph)_3$. Et_2O resulted in failure. Although aluminium alkyls have found extensive use for alkylations of metal halides and in fewer cases of metal oxo species, *e.g.* synthesis using $AlMe_3$ of WMe_6 from WCl_6 [23], $ReMe_6$ from $ReOMe_4$ [24], and $Re(O)Me_2(\eta\text{-}C_5Me_5)$ from $ReO_3(\eta\text{-}C_5Me_5)$ [25], aluminium aryls have been successfully employed twice, in the synthesis of the remarkably stable $Os(phenyl)_4$ [18b] and the synthesis of $ReO_3(mesityl)$ and $ReO_2(mesityl)_2$ from $ReO_3(OSiMe_3)$ and $Al(mesityl)_3(thf)$ (see Chapter 2).

(ii) 2-Methylphenyl

The interaction of $(Et_4N)[RuCl_5(solvent)]$ with five equivalents of 2-methylphenylmagnesium bromide in thf gives diamagnetic, air stable tetrakis(2-methylphenyl)ruthenium(IV) which can be crystallised from hexane or acetonitrile as fine red needles. The compound (Ru^{IV}, d^4) can also be obtained from the reaction of $(^nPr_4N)[RuO_4]$ or $Ru_2^{II}(\mu\text{-}O_2CMe)_4$ with excess Grignard in thf.

The ^1H n.m.r. spectrum has a singlet at δ 2.11 and multiplets at δ 6.85, 7.00 and 7.20 due to the aromatic hydrogens. The ^{13}C n.m.r. spectrum has seven sharp singlets as expected. The mass spectrum shows the parent ion, m/e 466 (84%), and subsequent losses of 2-methylphenyl groups; the base mass is at m/e 282 corresponding to Ru(2-methylphenyl)$_2^+$.

A diagram of the molecular structure [21] is shown in Figure 1.2; selected bond lengths and angles are given in Table 1.2.

The complex is isostructural with the osmium(IV) complex previously characterised[18], and has exact C(2) and $\bar{4}$ symmetry. Interestingly, we find that the two independent Ru-C distances show a slightly more pronounced difference than in the osmium complex (0.09Å here, 0.04 Å in the osmium complex). Otherwise, the average value for the Ru-C bond is essentially identical to that for the Os-C bond.

The only other examples of tetrahedral 2-methylphenyls are those of rhenium[21] (see Chapter 2) and osmium[18].

(iii) Mesityl

The interaction of $Ru_2(\mu\text{-}O_2CMe)_4$ with eight equivalents of mesitylmagnesium bromide in tetrahydrofuran leads to the diamagnetic tetrakis(2,4,6-trimethylphenyl)ruthenium(IV) as a red powder.

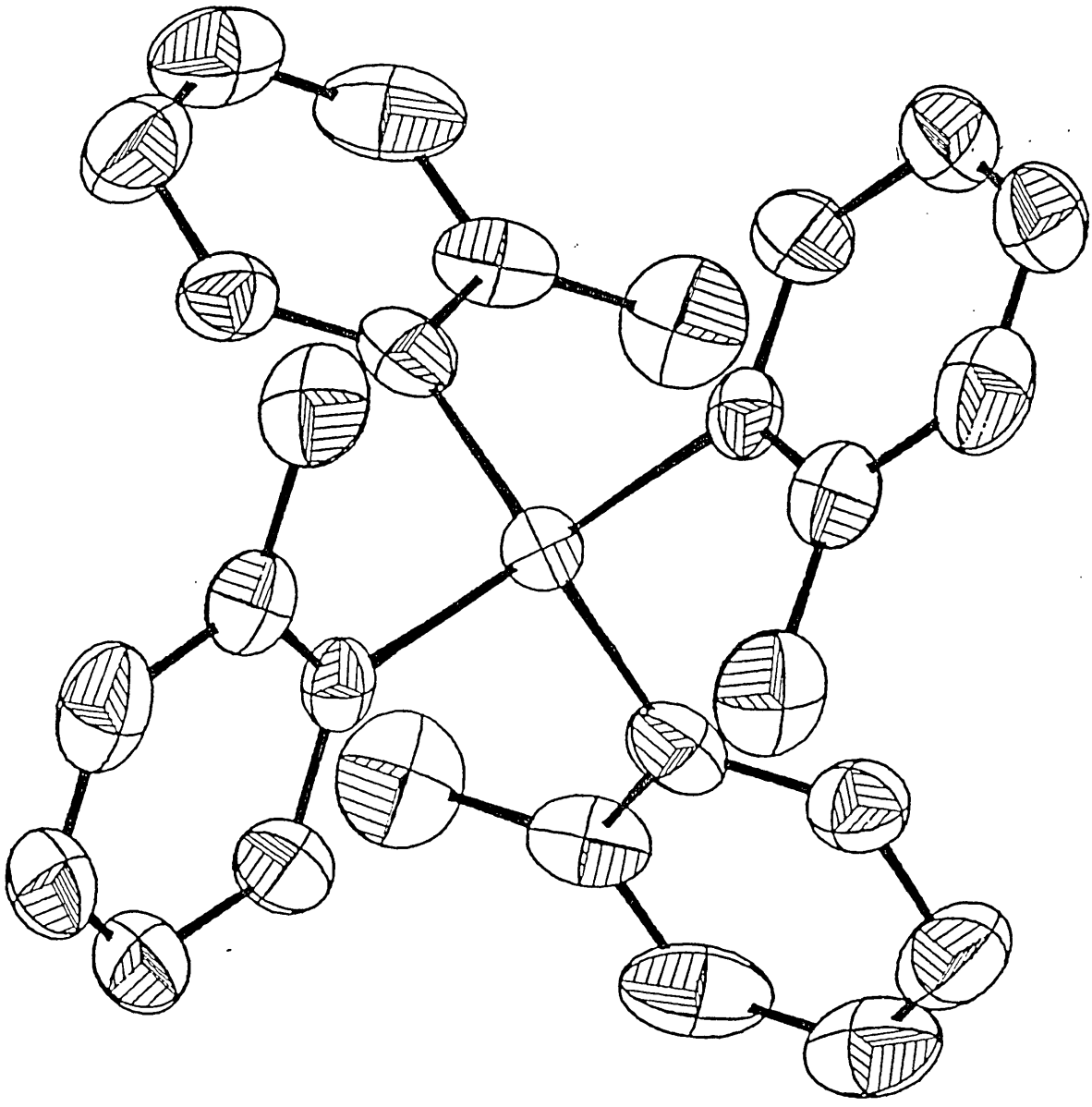


Figure 1.2: The molecular structure of $Re(2\text{-}MeC_6H_4)_4$.

Table 1.2: Bond lengths and angles for $Ru(2\text{-}MeC_6H_4)_4$.

Bond Lengths (Å) for $Ru(2\text{-}MeC_6H_4)_4$

C(1)-Ru	2.049(9)
C(7)-C(6)	1.538(13)
C(8)-Ru	1.931(10)
C(14)-C(13)	1.473(13)

Bond Angles (deg.) for $Ru(2\text{-}MeC_6H_4)_4$

C(8)-Ru-C(1)	106.5(3)
C(8)-Ru-C(1a)	107.4(4)
C(2)-C(1)-Ru	116.6(7)
C(9)-C(8)-Ru	119.0(7)
C(1)-Ru-C(1a)	114.6(6)
C(8)-Ru-C(8a)	114.4(6)
C(6)-C(1)-Ru	121.7(6)
C(13)-C(8)-Ru	125.6(7)

The reaction is clearly complicated, presumably involving a Ru-Ru bond cleavage and a disproportionation, possibly:

$$2Ru^{II} \longrightarrow Ru^{IV} + Ru^{O}$$

The i.r. spectrum shows mesityl bands while the ^1H n.m.r. spectrum has lowfield phenyl resonances at δ6.8 and two sharp singlets at δ2.24 and 2.19 (relative intensities 3:6H respectively). The mass spectrum at 70eV shows the parent ion, m/e 578 (4.1%), and subsequent losses of mesityl ligands, complicated further by the facile loss of methyl groups from the aromatic ring. The base peak, m/e 207, can be ascribed to $Ru(Me_2C_6H_2)^+$.

A number of well-characterised tetramesityl analogues are known, such as the homoleptic compounds of Ti [26], Cr [27] and Mo [28]. These compounds 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 [29] or *ortho*-hydrogen abstraction [30] pathways.

(iv) 2,6-Dimethylphenyl

The interaction of $(Et_4N)[RuCl_5(thf)]$ with five equivalents of 2,6-dimethylphenylmagnesium bromide in tetrahydrofuran gives diamagnetic tetrakis(2,6-dimethylphenyl)ruthenium(IV) as dark red crystals in low yield. The i.r. spectrum exhibits peaks due to the xylyl ligand and the ^1H n.m.r. spectrum shows peaks at δ7.11 and 6.90 (intensity 2:1 respectively) and one peak at δ2.13. The mass spectrum shows the parent ion m/e 522 (79%) and subsequent losses of the ligand, again complicated further by the facile loss of methyl groups.

(v) 4-*tert*-Butylphenyl

The reaction of $(Et_4N)[RuCl_5(thf)]$ with six equivalents of 4-*t*-butylphenylmagnesium bromide in tetrahydrofuran or diethyl ether gives diamagnetic tetrakis(4-*t*-butylphenyl)ruthenium(IV) as dark red powder in low yield. The ^1H n.m.r. spectrum shows the unsymmetrical *para*-disubstitution pattern for the aromatic ring and a sharp singlet for the *tert*-butyl protons. The $^{13}C-\{^1H\}$ n.m.r. spectrum consists of six sharp singlets; those at δ31.4 and 34.5 are due to the three methyl groups and the tertiary butyl group, respectively, while peaks at δ125.6, 126.7, 138.3 and 150.0 are due to the four unique phenyl carbons. The mass spectrum is complicated by the facile losses of the methyl groups from the 4-*t*-butyl groups. However, the spectrum shows all ruthenium aryl losses and peaks from the subsequent loss of methyl and butyl groups. The base mass, m/e 398, presumably corresponds to $Ru(^tBuC_6H_4)(C_6H_4)(C_6H_4C)^+$ or an equivalent formulation. The compound shows wide solubility in aliphatic and aromatic hydrocarbons and ethers but decomposes rapidly in air both in solution and in the solid state, presumably due to the absence of *ortho*-protecting groups on the aromatic ring.

Experimental

Microanalyses were by Pascher, Remagen and Imperial College Microanalytical Laboratories. Melting points were determined in sealed tubes under argon and are uncorrected.

Spectrometers: I.r., Perkin Elmer 683 (spectra in Nujol mulls or KBr discs in cm^{-1} between CsI plates); N.m.r., Bruker WM-250 (^1H n.m.r., 250.13 MHz; ^{13}C n.m.r., 62.90 MHz), Jeol FX90Q (^1H n.m.r., 89.55 MHz; ^{13}C n.m.r. 22.51 MHz), Bruker AM-500 (data in $CDCl_3$,

CD_3CN, C_6D_6 or C_7D_8 in p.p.m. relative to $SiMe_4$); M.s., V6 Micromass 7070 and Kratos M.S. 902 at 70eV;U.V., Perkin Elmer 551 in hexane.

X-ray crystallography: crystals of the compound were mounted under argon in Lindemann capillaries. All crystallographic measurements were made using a CAD4 diffractometer, operating in the ω-2ϑ scan mode with graphite monochromated M_0-K_a radiation (λ = 0.71069Å) in a manner previously described [31]. The structures were solved *via* the heavy atom method and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically and hydrogens, all of which were experimentally located on difference maps, isotropically.

All manipulations were carried out *in vacuo* or under argon. Solvents were distilled under argon from sodium-benzophenone (hexane, diethyl ether, thf, dioxane), sodium (toluene), calcium hydride (dichloromethane, acetonitrile) and degassed prior to use.

The compounds $Ru_2(O_2CMe)_4Cl$ [32], $Ru_2(O_2CMe)_4$ [33], $(Et_4N)[RuCl_5(MeCN)]$ [34], and $(^nPr_4N)[RuO_4]$ [35] were prepared by literature methods. Literature routes were also used for alkylating agents [36] and PMe_3 [37].

New compounds and analysis are given in Table 1.3.

Tetraethylammonium pentachloro(tetrahydrofuran)ruthenate(IV)

The salt $(Et_4N)[RuCl_5(MeCN)]$ (1.0 g, 2.2 mmol) was refluxed in thf (80 cm^3) for *ca.* 1 d. The solid was collected and washed with thf (2 × 30 cm^3) to yield a red brown solid.

Yield: 0.83 g, 79%; m.p. 156°C dec. [Found: C, 29.6; H, 5.6; N, 3.0%, $C_{12}H_{28}Cl_5NORu$ requires C, 30.0; H, 5.9; N, 2.9%].

I.r.: 2980s, 2950sh, 2905sh, 2878sh, 1480s, 1455s, 1391s, 1370m, 1345w, 1305w, 1185s, 1175s, 1068m, 1020s, 1005s, 920m, 865vs, 790s, 690w

Table 1.3: Properties and Analytical Data for Ruthenium Alkyl and Aryl Compounds

Compound	Colour	M.p.(ϑ_c/°C)	Analysis (%)[a]	
			C	H
$Ru(C_6H_{11})_4$	red-orange	*ca.* 150 dec.[b]	66.6 (66.5)	10.3 (10.2)
$Ru(2\text{-}MeC_6H_4)_4$	dark red	161-163	72.2 (72.2)	6.1 (6.1)
$Ru(2,4,6\text{-}Me_3C_6H_2)_4$	dark red	207 dec.[b]	74.4 (74.8)	7.3 (7.6)
$Ru(2,6\text{-}Me_2C_6H_3)_4$	dark red	182	73.4 (73.7)	6.9 (7.0)
$Ru(4\text{-}t\text{-}BuC_6H_4)_4$	dark red	82-84 dec.[b]	75.7 (75.8)	8.1 (8.3)

a found (required)

b decomposition without melting

and 470m.

1.1) Tetrakis(cyclohexyl)ruthenium(IV)

To a stirred solution of $Ru_2(O_2CMe)_4Cl$ (1.0 g, 2.11 mmol) in thf (50 cm^3) at -78°C was added cyclohexylmagnesium bromide (16.9 cm^3 of a 1.0 mol dm^{-3} solution in Et_2O, 16.9 mmol) and the mixture warmed up to 0°C. After *ca.* 1h. the volatile material was removed under reduced pressure and the residues extracted with hexane (2 × 30 cm^3). Concentration of the filtered extracts to *ca.* 25 cm^3 and cooling overnight (-20°C) afforded a red-orange crystalline solid.

Yield: 0.14 g, 15%.

I.r.: 1320br, 1280s, 1240s, 1024sh, 1005m, 970s, 820m and 790s.

N.m.r. ^1H: 2.62 (1H, m, α-H) and 1.58 (10H, mbr, β-, γ- and δ-H); ^{13}C, 49.74, 33.50, 27.46 and 26.73 (s, C_6H_{11}).

Mass Spectrum: m/e 436 (42%), $^{104}RuR_4^+$, 434 (80%) $^{102}RuR_4^+$, 433 (47%) $^{101}RuR_4^+$, 432 (40%) $^{100}RuR_4^+$, 431 (31%) $^{99}RuR_4^+$, 428 (15%) $^{96}RuR_4^+$, 184 (25%) RuR^+, 83 (13%) $C_6H_{11}^+$.

1.2) Tetrakis(2-methylphenyl)ruthenium(IV)

Method A - To a stirred suspension of $(Et_4N)[RuCl_5(MeCN)]$ (0.43 g, 0.96 mmol) in thf (50 cm^3) at -78°C was added 2-methylphenyl magnesium bromide (2.3 cm^3 of a 1.6 mol dm^{-3} solution in Et_2O, 3.8 mmol) and the mixture warmed to room temperature then refluxed for 2 h. The volatile material was removed and the residue extracted in diethyl ether (3 × 30 cm^3). Water (10 cm^3, degassed for 1 h) was added to destroy any excess Grignard, and the red ether solution filtered onto $MgSO_4$ (5 g) at -10°C. Filtration and evaporation to dryness, extraction into hexane (10 cm^3) and cooling overnight (-20°C) yields a dark red crystalline solid. Yield: 0.15 g, 34%.

Method B - As above except using $(Et_4N)[RuCl_5(thf)]$.

Yield: *ca.* 48%.

Method C - To a stirred suspension of $Ru_2(\mu\text{-}O_2CMe)_4$ (o.27 g, 0.62 mmol) in thf (50 cm^3) at -78°C was added 2-methylphenylmagnesium bromide (3.0 cm^3 of a 1.6 mol dm^{-3} solution in Et_2O, 4.9 mmol); work up as Method A. Yield: 0.07 g, 24%.

Method D - To a stirred suspension of $(^nPr_4N)[RuO_4]$ (0.22 g, 0.63 mmol) in thf (30 cm^3) at -78°C was added 2-methylphenylmagnesium bromide (2.3 cm^3 of a 1.9 mol dm^{-3} solution in Et_2O, 4.39 mmol); work up as Method A. Yield: 0.12g, 41%.

Mass Spectrum: m/e 466 (84%) $Ru(2\text{-}MeC_6H_4)_4^+$, 374 (12%) $Ru(2\text{-}MeC_6H_4)_3^+$, 282 (100%) $Re(2\text{-}MeC_6H_4)_2^+$, 192 (12%) $Ru(2\text{-}MeC_6H_4)_1^+$, 91 (55%) $C_7H_7^+$.

I.r.: 1565s, 1435sh, 1255w, 1190m, 1160w, 1050w, 1025s, 979w, 865w, 740vs, 660m, 500w and 445s.

N.m.r. ^1H: 2.11 (3 H, s, 2-Me), 6.85 (1 H, m, C_6H_4), 7.00 (2 H, m, C_6H_4) and 7.20 (1 H, m, C_6H_4).

^{13}C: 25.3 (s, 2-Me) and 124.8, 127.3, 128.9, 133.4, 139.0, 160.8 (s, C_6H_4).

U.v.: λ = 437, 476 and 574 nm.

(ϵ = 3218, 2484 and 2190 respectively).

1.3) Tetrakis(2,4,6-trimethylphenyl)ruthenium(IV)

To a stirred suspension of $Ru_2(\mu\text{-}O_2CMe)_4$ (0.42 g, 0.96 mmol) in thf (40 cm^3) at -78°C was added mesitylmagnesium bromide (12.8 cm^3 of a 0.6 mol dm^{-3} solution in Et_2O, 7.66 mmol). The mixture was warmed slowly and stirred at room temperature for 1 h. The resulting red solution was evaporated and the residue extracted into hexane (3 × 30 cm^3), and the solution filtered and evaporated. The residues were extracted

with diethyl ether (2 × 30 cm^3) and H_2O (20 cm^3) added, the mixture stirred for 0.5h., cooled to -10°C and filtered onto $MgSO_4$ (5 g). The red solution was stirred for 1 h., filtered, concentrated and the residue extracted with hexane (10 cm^3) and cooled overnight (-20°C) to yield a red solid. Yield: 0.12 g, 21%.

Mass Spectrum: m/e 578 (4%) $Ru(mesityl)_4^+$, 341 (10%) $Ru(mesityl)_2^+$, 221 (22%) $Ru(mesityl)_1^+$, 207 (100%) $Ru(mesityl-Me)_1^+$, 119 (4%) $mesityl^+$, 91 (29%) $C_7H_7^+$, 77 (15%) $C_6H_5^+$.

I.r.: 1582w, 1305m, 1260m, 1085vbr, 1030vbr, 805m, 608w, 540w and 530w.

N.m.r. ^1H: 2.24 (3H, s, *p*-MeC_6H_2), 2.19 (6H, s, *o*-MeC_6H_2) and 6.8 (2H, s, phenyl protons).

1.4) Tetrakis(2,6-dimethylphenyl)ruthenium(IV)

Method A - To a stirred suspension of $(Et_4N)[RuCl_5(thf)]$ (0.35 g, 0.73 mmol) in thf (40 cm^3) at -78°C was added 2,6-dimethylphenylmagnesium bromide (11.6 cm^3 of a 0.5 mol dm^{-3} solution in Et_2O, 5.8 mmol) and the mixture was warmed to room temperature and stirred for *ca.* 1 d. The volatile material was removed under reduced pressure and the residue extracted in diethyl ether (3 × 30 cm^3). Water (20 cm^3, degassed for 1 h.) was added, stirred for 1 h., and the dark red ether solution was filtered onto $MgSO_4$ (5 g) at -10°C. Filtration and concentration to dryness, extraction into hexane (10 cm^3) and cooling overnight (-20°C) yields dark red crystalline solid. Yield: 0.08 g, 21%.

Method B - As Method A, except using $(Et_4N)[RuCl_5(MeCN)]$ instead of the tetrahydrofuran adduct. Yield: 0.05 g, 13%.

Mass Spectrum: m/e 522 (79%) $Ru(2,6\text{-}Me_2C_6H_3)_4^+$, 415 (27%)

$Ru(2,6\text{-}Me_2C_6H_3)_3^+$, 309 (100%) $Ru(2,6\text{-}Me_2C_6H_3)_2^+$, 205 (34%) $Ru(2,6\text{-}Me_2C_6H_3)_1^+$, 106 (43%) $2,6\text{-}Me_2C_6H_3)_2^+$, 91 (70%) $C_7H_7^+$, 77 (30%) $C_6H_5^+$.

I.r.: 1556w, 1375sh, 1305m, 1265m, 1161br, 1153m, 1020s, 978m. 897w, 802br, 768s, 605m, and 510m.

N.m.r. ^1H: 2.13 (6H, s, $Me_2C_6H_3$), 6.90 (1H, m, *p*-Hydrogen) and 7.11 (2H, m, *m*-Hydrogen).

1.5) Tetrakis(4-*tert*-butylphenyl)ruthenium(IV)

To a stirred suspension of $(Et_4N)[RuCl_5(thf)]$ (0.3 g, 0.63 mmol) in diethyl ether (40 cm^3) at -78°C was added 4-*tert*-butylphenylmagnesium bromide (4.8 cm^3 of a 0.78 mol dm^{-3} solution in Et_2O, 3.75 mmol) and the mixture warmed to room temperature and stirred for 8 h. The red solution was filtered and H_2O (25 cm^3) added, stirred and filtered onto $MgSO_4$ (8 g) at -10°C. Filtration and concentration to dryness, extraction into hexane (25 cm^3) and cooling overnight at -20°C yields a dark red solid. Yield: 0.08g, 20%.

Mass Spectrum: m/e 634 (7%) $Ru(^tBuC_6H_4)_4^+$, 501 (8%) $Ru(^tBuC_6H_4)_3^+$, 368 (18%) $Ru(^tBuC_6H_4)_2^+$, 234 (4%) $Ru(^tBuC_6H_4)^+$, 90 (58%) $C_7H_5^+$, 57 (44%) CMe_3^+.

I.r.: 2964s, 2904sh, 2872sh, 1601w, 1494w, 1461w, 1400w, 1362m, 1262vs, 1297vbr, 1021vbr, 865sh, 801vs, 702w, 664sh, 557w and 397s.

N.m.r. ^1H: 1.41 (9H, s, Bu^t), 7.53 (4H, m, C_6H_4).

^{13}C: 31.4 (*s*, CMe_3), 34.5 (*s*, CMe_3), 125.6, 126.7, 138.3 and 149.9 (*s*, C_6H_4).

CHAPTER 2

HOMOLEPTIC ARYL AND OXO-ARYL COMPOUNDS OF RHENIUM

HOMOLEPTIC ARYL AND OXO-ARYL COMPOUNDS OF RHENIUM

Introduction

Although an in depth discussion on homoleptic alkyls and aryls of transition metals was given in the introduction and in Chapter 1, it is worth reiterating that no homoleptic aryl compounds of rhenium were known until the present study. Dodeca(alkyl)triangulo-trirhenium(IV) compounds have been known since 1977 [38], (*e.g.* Re_3R_{12} where R = Me, CH_2SiMe_3, CH_2CMe_2Ph and CH_2CMe_3). Recently, the X-ray diffraction study of the mixed alkyl $Re_3(\mu\text{-Me})_3(CH_2Ph)_6$ has been determined [39], as well as the synthesis of numerous triangulotrirhenium(III) and -(IV) cluster alkyls *e.g.* $Re_3(\mu\text{-Cl})_3R_6$, (R = Me, CH_2SiMe_3, CH_2Ph, C_6H_5, 4-MeC_6H_4)[38,40,41] $Re_3(\mu\text{-Me})_3R_6$ (R = Me, CH_2SiMe_3)[38,41] including some phosphine and pyridine [38,41] adducts of these.

Within group VII, various homoleptic alkyl derivatives of manganese are accessible, but these are mostly divalent. Reaction of $MnCl_2$ with appropriate Mg(R)X or MgR_2 gives, for example, $[Mn(CH_2SiMe_3)_2]_n$, $[Mn(CH_2CMe_3)_2]_4$ and $[Mn(CH_2CMe_2Ph)_2]_2$ which all have subtly different oligomeric structures [42]. If excess 1-norbornyl-lithium is added to $MnBr_2$, the green tetravalent $Mn(1\text{-norbornyl})_4$ complex is the unusual result [43]. Whether oxidation is the result of disproportionation of MnR_2 or adventitious oxygen is not clear; certainly action of O_2 on $[Mn(CH_2SiMe_3)_2]_n$ yielded solutions of a non-isolable species formulated as $Mn(CH_2SiMe_3)_4$ [42,44,45] on the basis of similarity of colour and E.S.R. characteristics to those of $Mn(1\text{-norbornyl})_4$.

The richest chemistry among the triad undoubtedly belongs to rhenium. The first publication on rhenium oxo-alkyls appeared in

1975 and contained the synthesis of the paramagnetic rhenium(VI) complexes $ReOR_4$, R = Me, CH_2SiMe_3, and the diamagnetic dimer $Re_2O_3(CH_2SiMe_3)_6$[46,24]. Electron spin resonance [47] and photoelectron spectra [48] properties were reported separately and oxidation reactions with NO and dry air led to the isolation of the compounds *cis*-ReO_2Me_3 [24] and ReO_3Me [49] respectively, and opened the way to the limited and valuable class of rhenium(VII) oxo-alkyls (d^0 systems).

Since then, a large number of rhenium oxo-alkyls have been produced [19a] along with a quantity of rhenium(V) solvated magnesium and lithium compounds, *e.g.* $[Me_4ReO]_2Mg(thf)_4$, $[Me_4ReO]Li(thf)_2$, $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$ and $\{[o\text{-}(CH_2)_2C_6H_4]_2ReO\}_2Mg(thf)_4$.

Recently, high oxidation state oxo-aryl compounds of rhenium have been isolated and characterised. However, some reactions which could have led to rhenium(V) oxo-aryls - by using the rhenium(V) starting materials $ReOCl_3(PR_3)_2$ or $ReO(OR)Cl_2(PR'_3)_2$ with lithium alkylating agents - have been tried by J. Chatt and co-workers and yielded a number of reduced rhenium(III) and -(II) aryls [50], of the type $ReR_3(PR_3)_2$ and $[ReR_2(PR'_3)_2]_n$ respectively. The most celebrated complex in this group, $RePh_3(PEt_2Ph)_2$, has been structurally investigated [51] to reveal a trigonal bipyramidal arrangement with the equatorial phenyl groups and the phosphines in the axial positions.

Among the very rare class of metal oxo-aryls the best characterised members are those of vanadium [52], molybdenum [53] and osmium compounds (see Chapter 3).

Relatively simple starting materials were employed to produce the first examples of rhenium(V) and -(VI) oxo-aryls; the thermal stability of these is critically dependent on the presence of *ortho*-substituents on the aromatic ring and the nature of the product obtained is determined by whether a di-*ortho* or mono-*ortho*-substituted

phenyl group is used. Examples of the di-*ortho*-substituted phenyl group include $ReO_2(mesityl)_2$, $[ReO_2(mesityl)_2]_2Mg(thf)_2$ from Re_2O_7 or $(Me_3NH)[ReO_4]$ and $ReO(mesityl)_4$ from $ReOCl_4$ [19b] whereas the mono-*ortho*-substituted rings yield only $ReOR_4$, R = 2-methylphenyl and 2-methoxyphenyl [19b] from $(Me_3NH)[ReO_4]$, Re_2O_7 or $ReOCl_4$.

In this chapter, the first example of a rhenium homoleptic aryl has been prepared and its rich reaction chemistry has been investigated. Further examples of high oxidation state rhenium(V) and -(VI) oxo-aryls are also presented as well as the first example of a rhenium(VII) oxo-aryl, $ReO_3(mesityl)$.

Analytical data for the new compounds are listed in Table 2.1.

Results and Discussion

(A) (i) Tetrakis(2-methylphenyl)rhenium(IV)

The interaction of $ReCl_4(thf)_2$ with 2.4 equivalents of 2-methylphenylmagnesium bromide in tetrahydrofuran under argon yields a deep red solution, from which dark red crystals of the paramagnetic compound $Re(2\text{-}MeC_6H_4)_4$ can be obtained in low yield after extraction into hexane and subsequent recrystallisation. The addition of four equivalents of Grignard gives a deep purple solution from which came oily material - no product could be crystallised from toluene or tetrahydrofuran.

The i.r. spectrum shows only peaks characteristic of the 2-methylphenyl ligand with no peaks due to Re-C evident. The mass spectrum shows two parent ions, m/e 551 (18%) for ^{187}Re and 549 (11%) for ^{185}Re, together with ions due to subsequent loss of 2-methylphenyl ligands, with high intensities for both isotopes. The base peak is the tropylium ion, m/e 91, $C_7H_7^+$. No higher mass peaks were observed indicating that the compound is monomeric, and not the trimer, *i.e.*

Table 2.1: Physical and analytical properties of aryl and oxo-aryl rhenium compounds

Compound	Colour	M.p.(°C)	Analysis (%) [a]					
			C	H	O	N	Cl	Re
$Re(2\text{-}MeC_6H_4)_4$	black/red	138-140	60.5 (61.0)	5.2 (5.1)				
$ReO(2\text{-}MeC_6H_4)_4$	blue/green	147-149	59.2 (59.3)	5.0 (5.0)	2.7 (2.8)			
$Re(NO)(2\text{-}MeC_6H_4)_2$	red	126-128	40.6 (42.2)	3.27 (3.5)		3.31 (3.5)		
$ReCl(2\text{-}MeC_6H_4)_2$	red	90-92	38.2 (41.6)	3.4 (3.4)			10.1 (8.8)	
$Re(^tBuN)_2(CO\text{-}2\text{-}MeC_6H_4)_2$ [b]	green	66-67	54.8 (50.9)	6.6 (5.7)		5.9 (4.9)		
$(BF_4)[Re(2\text{-}MeC_6H_4)_4]$ [b]	purple	232 [c]	d					
$[ReO_2(xylyl)_2]_2Mg(thf)_2$	purple	132	47.0 (46.9)	5.2 (5.1)	9.8 (9.4)			
$ReO_2(xylyl)_2$	red	138-140	44.8 (44.8)	4.4 (4.2)	7.4 (7.5)			43.9 (43.5)

Table 2.1 continued...

Table 2.1 continued.....

Compound	Colour	M.p. (°C)	Analysis (%) [a]					
			C	H	O	N	Cl	Re
$ReO_2(mesityl)_2$	red	194-196	47.3 (47.4)	4.8 (4.8)	7.0 (7.0)			
$ReO_3(mesityl)$	red	111-112	31.5 (30.6)	3.1 (3.1)	13.0 (13.6)			

[a] Found (required)

[b] postulated compounds

[c] sublimes

[d] no reasonable data could be obtained before publication.

dodeca(2-methylphenyl)triangulotrirhenium(IV). In the mass spectrum of $Re_3(CH_2SiMe_3)_{12}$ the triangulotrirhenium core remained intact and fragmentations due to the sequential loss of CH_2SiMe_3 groups were seen [38].

$$Re_3R_8^+ \longrightarrow Re_3R_7^+ \longrightarrow Re_3R_6^+$$

The magnetic moment of $Re(2\text{-}MeC_6H_4)_4$, μ_{eff} = 1.31 B.M., is in accordance with low spin Re^{IV}, d^3, with one unpaired electron. The e.s.r. spectrum in frozen solution (98K) shows a poorly resolved extremely broad signal over the range 150-380 mT, on which is superimposed the spectrum of $ReO(2\text{-}MeC_6H_4)_4$ formed by oxidation [19b]; we have been unable to obtain a spectrum without this impurity due to the extreme air sensitivity of $Re(2\text{-}MeC_6H_4)_4$. Similar problems were encountered with the e.s.r. spectrum of the postulated "$Re(CH_2SiMe_3)_4$" compound, believed to be formed in the reaction of $ReCl_4(thf)_2$ with trimethylsilylmethylmagnesium chloride before the intermediate compound trimerises to $Re_3(CH_2SiMe_3)_{12}$ [38]. However, the tetraaryl compound shows sharp ^1H and ^{13}C n.m.r. spectra, evidently due to a quirk of relaxation times. The ^1H n.m.r. spectrum shows a singlet at δ2.39 due to the methyl hydrogens and two multiplets at δ7.20 and 7.28, for the aromatic hydrogens; the $^{13}C\text{-}\{^1H\}$ n.m.r. shows seven sharp singlets for all seven unique carbon atoms.

The structure of the compound has been determined by X-ray crystallography and a diagram of the molecular structure is shown in Figure 2.1; selected bond lengths and angles are given in Table 2.2. The rhenium coordination is slightly distorted tetrahedral and although the molecule lies in a general position in the unit cell, Figure 2.2 shows the packing in the unit cell viewed along the C-axis;

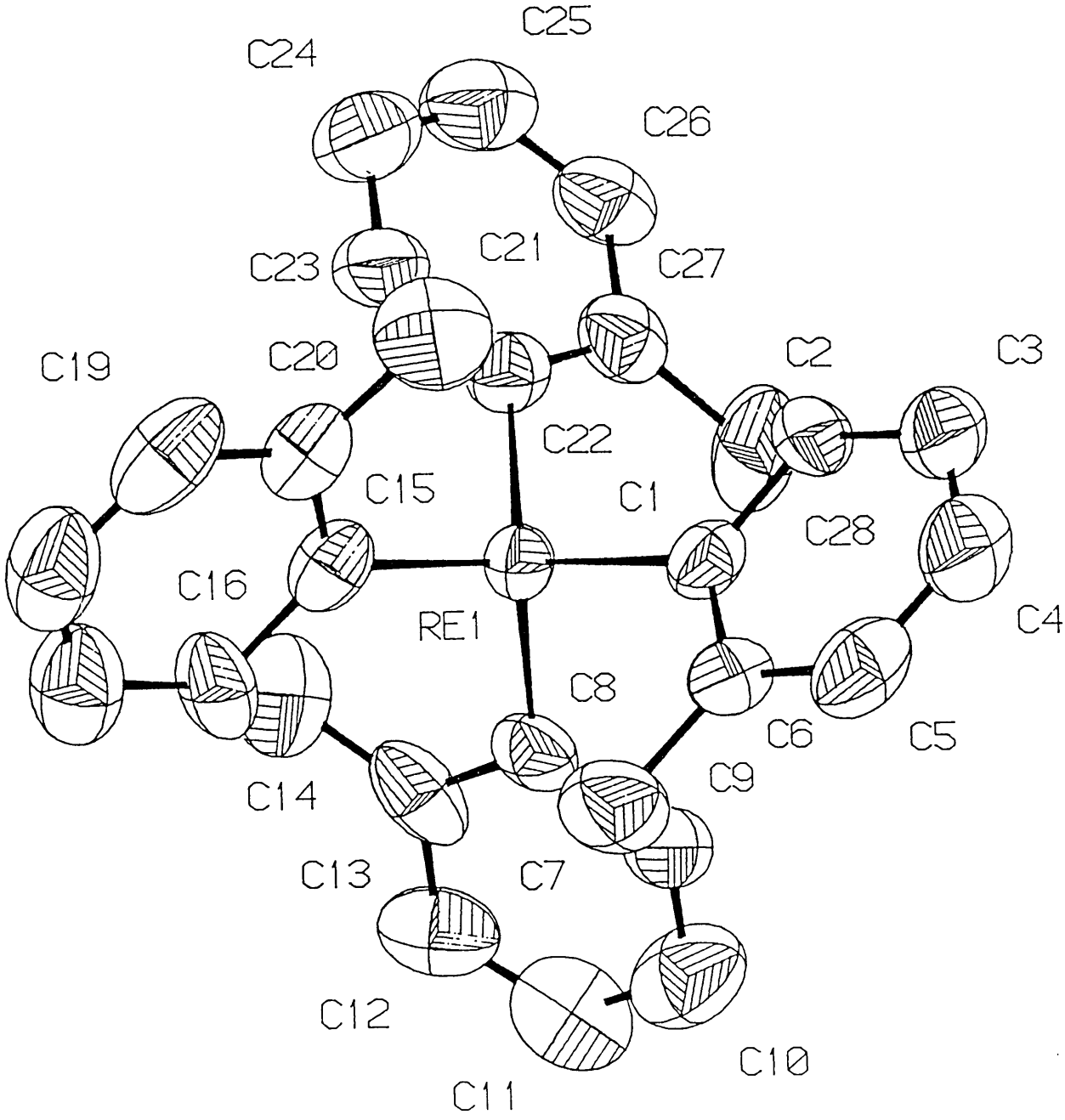


Figure 2.1: The molecular structure of $Re^{IV}(2\text{-}MeC_6H_4)_4$.

Table 2.2: Selected bond lengths (Å) and angles (deg.) for $Re^{IV}(2\text{-}MeC_6H_4)_4$.

Bond Lengths

Re-C(1)	2.020
Re-C(8)	2.038
Re-C(15)	2.033
Re-C(22)	2.028
C(6)-C(1)	1.412
C(7)-C(6)	1.509

Bond Angles

C(8)-Re-C(1)	108.9
C(15)-Re-C(8)	113.4
C(22)-Re-C(8)	107.4
C(15)-Re-C(1)	105.6
C(22)-Re-C(1)	112.4
C(22)-Re-C(15)	109.3
C(6)-C(1)-Re	122.1
C(6)-C(1)-C(2)	117.9
C(7)-C(6)-C(1)	120.4

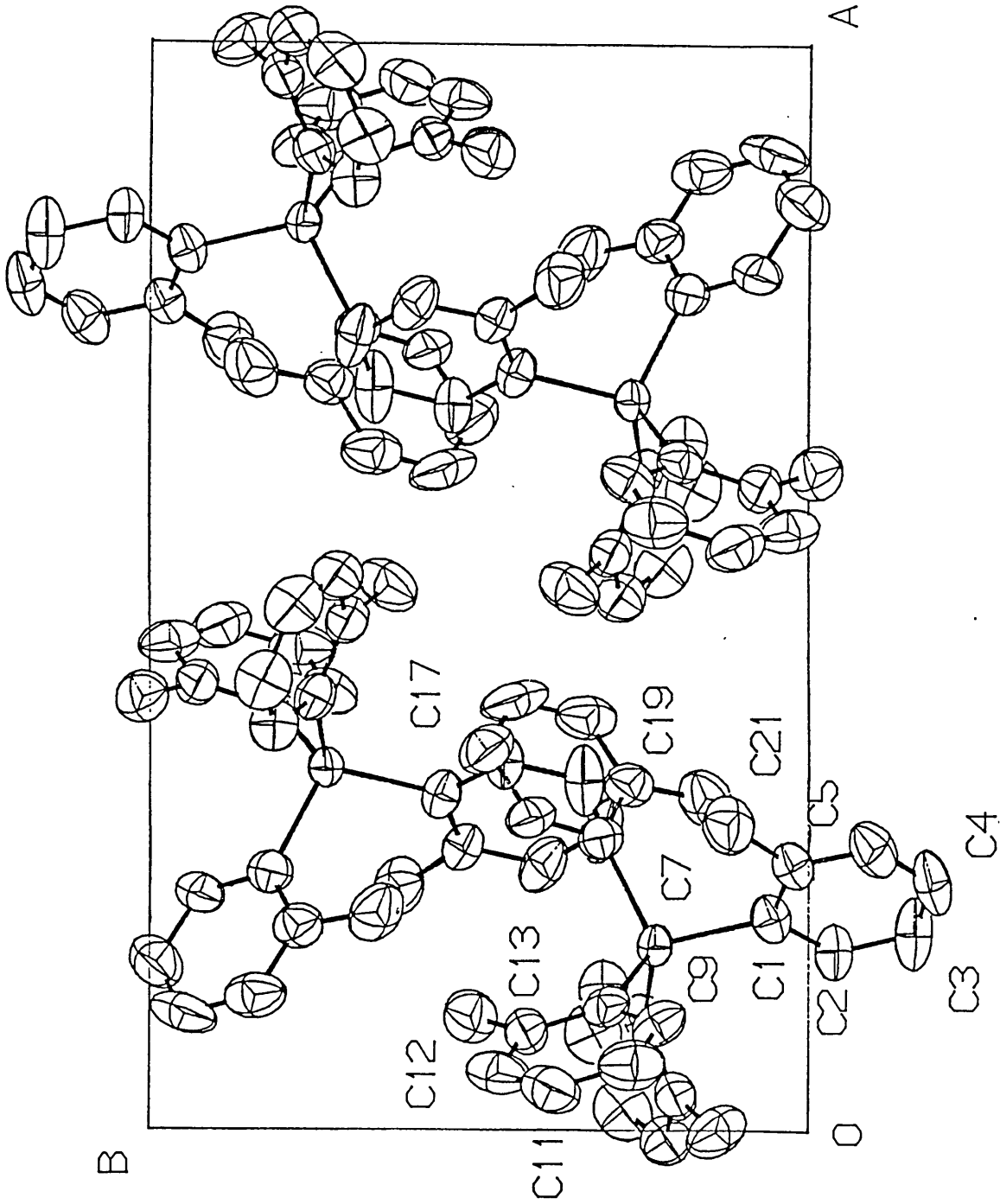


Figure 2.2: The unit cell of $Re(2\text{-}MeC_6H_4)_4$.

the molecular symmetry is quite close to $\bar{4}$. A similar structure was found for the osmium[18b] and ruthenium [21] analogues (see Chapter 1), the molecules of which, however, occupy a special position in the cell; Figure 2.3 shows the packing in the unit cell of $Ru(2\text{-}MeC_6H_4)_4$ viewed along the C-axis. The main difference between the Re and Os/Ru structures is that whereas with Os/Ru there is a small degree of flattening of the tetrahedron in the direction of the $\bar{4}$ axis (C-Os-C' angles ≈ 114, 117°), in the rhenium complex there is essentially no distortion of this type, but a slight twist of the two C-Re-C planes, which make a dihedral angle of 86.8°.

Reactions of $Re(2\text{-}MeC_6H_4)_4$

(ii) Synthesis and structure of oxotetrakis(2-methylphenyl)rhenium(VI)

As noted above $Re(2\text{-}MeC_6H_4)_4$ on air oxidation gives air stable, paramagnetic dark green crystals of $ReO(2\text{-}MeC_6H_4)_4$. This compound can also be made by the addition of H_2O_2. The compound can be crystallised from acetone or light petroleum, and is soluble in halogenated hydrocarbons, aromatic and aliphatic hydrocarbons, ethers and acetonitrile but is insoluble and unaffected by water. The i.r. spectrum shows analogous features to those observed for $ReO(mesityl)_4$, having a ν(Re=O) stretch[19b] at 992 cm^{-1} with a shoulder at 982 cm^{-1} probably due to aggregated species in the lattice. The mass spectrum fails to show the parent ion, however peaks at m/e 385 (99%) $^{187}ReOR_2^+$ and 383 (100%) $^{185}ReOR_2^+$ are observed, the parent molecule obviously losing 2,2'-dimethylbiphenyl, m/e 182 (8%). Peaks due to isotopes of ReR_2^+, $ReOR^+$ and ReR^+ are also observed.

The X-ray structure has been determined [21] and is shown in

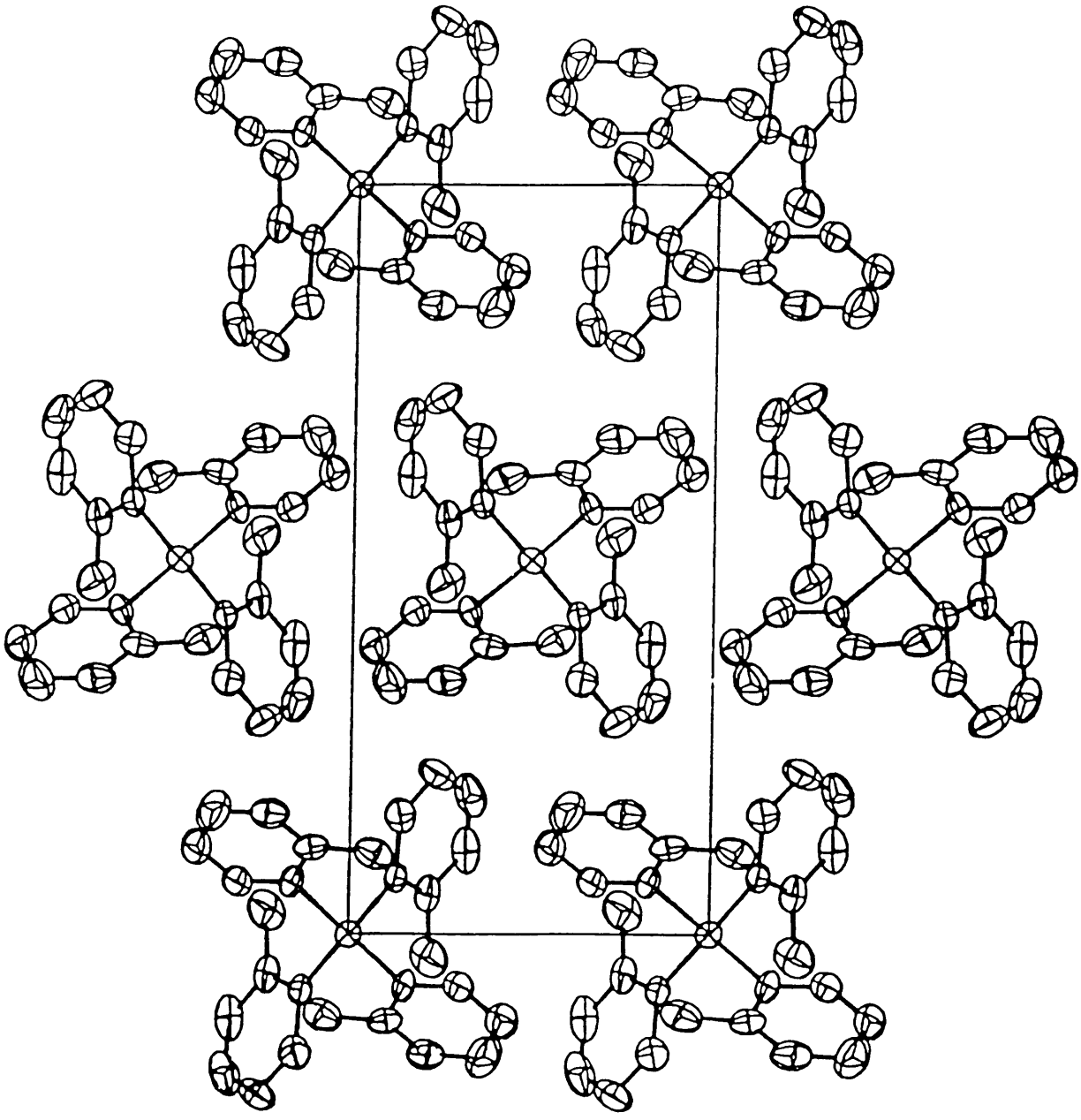


Figure 2.3: The unit cell of $Ru(2\text{-}MeC_6H_4)_4$.

Figure 2.4; selected bond lengths and angles are given in Table 2.3. The molecule lies on a four-fold axis in the unit cell and as a result all four 2-methylphenyl rings have equivalent orientations, with the methyl groups on the same side of the oxo function. The contact distances between the oxo atom and the methyl carbon are 3.106Å, and the CH_3 group is orientated so that one hydrogen is closer to the oxygen (2.633Å) than the other two. It is possible that this is indicative of electrostatic interaction, although there is a clear indication that the ring is tilted slightly to relieve this close contact (*c.f.* angles Re-C(1)-C(2), Re-C(1)-C(6), Table 2.3). It is also worth noting that the phenyl ring angle at the point of bonding to the metal (C(2)-C(1)-C(6)) is significantly less than 120°. The Re=O and Re-C distances are similar to those found in $ReO(mesityl)_4$ [19b].

(iii) Synthesis of nitrosobis(2-methylphenyl)rhenium(III)

The reaction of nitric oxide with the tetraaryl in hexane at room temperature yields red semi-crystalline material of the title compound. The i.r. shows a strong peak at 1642 cm^{-1} indicating a nitrosyl group. Recent X-ray studies [54] have revealed the presence of linear and bent M-NO groups:

M-N≡O: M-N=O:

I II

indicating that the nitrosyl groups in (I) and (II) are regarded as NO^+ and NO^- respectively. Due to the value of ν(NO) we tentatively assign a bent geometry with a negative charge. No parent ion could be detected in the mass spectrum but the familiar peaks of biphenyl

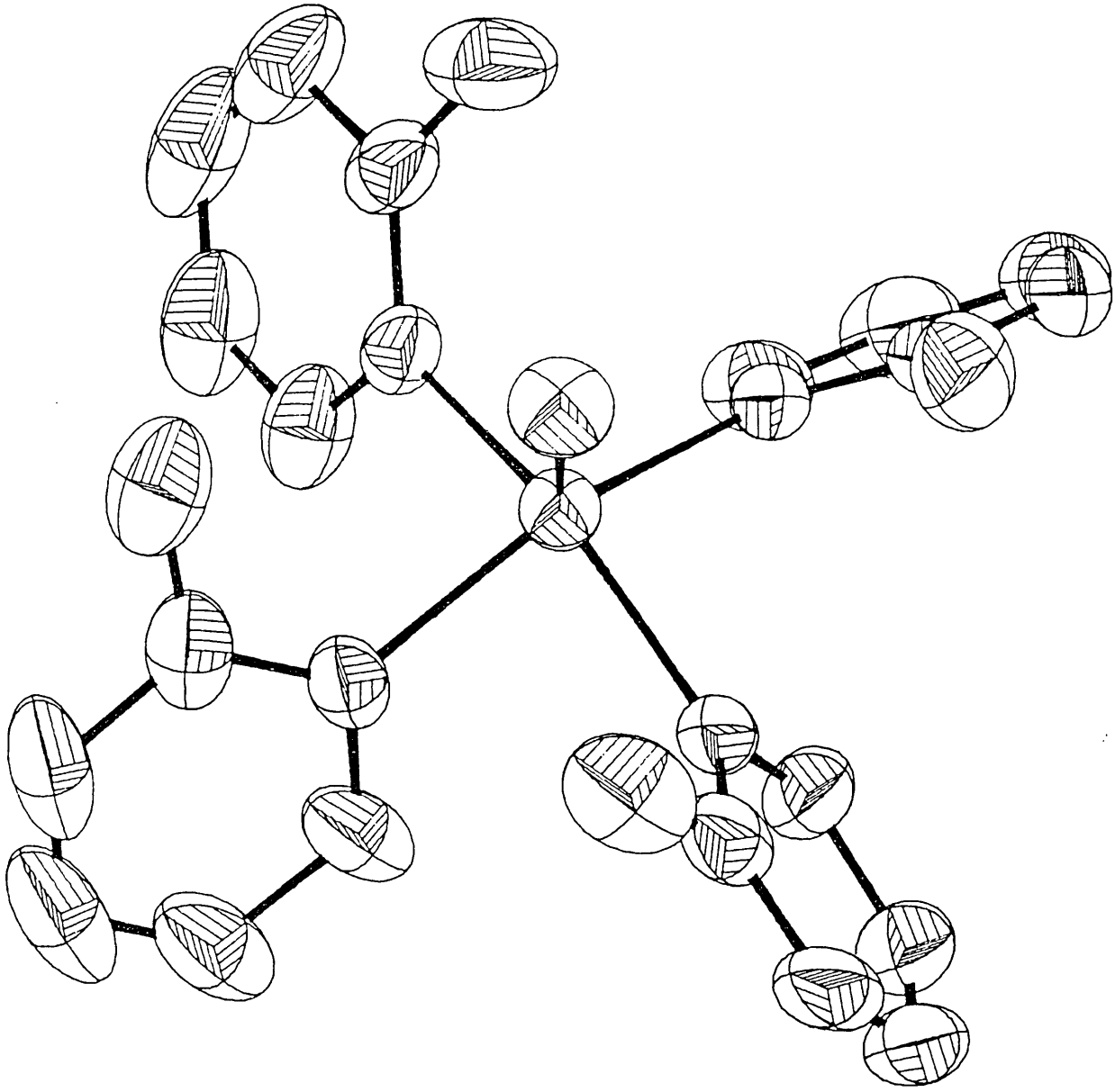


Figure 2.4: The molecular structure of $ReO(2\text{-}MeC_6H_4)_4$.

Table 2.3: Bond lengths (Å) and angles (deg.) for $Re^{VI}O(2\text{-}MeC_6H_4)_4$.

Bond Lengths

Re-O	1.830
Re-C(1)	2.067
C(1)-C(2)	1.404
C(6)-C(7)	1.541
C(2)-C(3)	1.394

Bond Angles

O-Re-C(1)	105.98
C(1)-Re-C(15)	148.04
C(1)-Re-C(8)	85.65
C(1)-C(2)-C(3)	120.18
Re-C(1)-C(2)	118.53
Re-C(1)-C(6)	124.04
C(2)-C(1)-C(6)	117.13

and the tropylium ion are observed. The ^1H n.m.r. spectrum shows the characteristic *o*-tolyl peaks.

(iv) Synthesis of Chlorobis(2-methylphenyl)rhenium(III)

Addition of chlorine to the tetraaryl in hexane at -78°C immediately precipitated a red powder. The air-sensitive compound was washed with ether and hexane and dried *in vacuo*. Decomposition in chlorinated solvents and solubility difficulties made the ^1H n.m.r. difficult to obtain, however a sharp singlet at δ2.00 and multiplets for the aromatic hydrogens are observed. The mass spectrum shows peaks due to biphenyl and the base mass is the tropylium ion m/e 91, $C_7H_7^+$.

(v) Miscellaneous reactions

Although $Re(2\text{-}MeC_6H_4)_4$ does not react with other small gases (H_2,CO, SO_2 and CO_2),the action of H_2S causes immediate decomposition to a grey insoluble precipitate and a colourless solution. The reaction of lithium aluminium hydride over 24h. gave a white tetrahydrofuran soluble powder, with broad peaks in the i.r. and a melting point of more than 340°C.

Reactions also occurred with ethylene and ethylene sulphide; in both instances the solutions turned from black to bright red, however the resulting compounds could not be identified.

Prolonged refluxing in hexane with *tert*-butylisocyanate once led to a green solution from which green powder could be isolated when cooled overnight. The compound shows an acyl band in the i.r. spectrum at 1642 cm^{-1}, and mass spectral evidence shows the base peak at m/e 119 due to $OCC_6H_4Me^+$. Nitrogen analysis suggests two nitrogen atoms per molecule. The compound is diamagnetic, showing clean ^1H and

^{13}C n.m.r. spectra implying that the compound is Re^{V}, d^2 or Re^{VII}, d^0. The ^{1}H n.m.r. spectrum shows the familiar peaks at δ2.40 (relative intensity 6H) and multiplets at δ7.22 and 7.31 due to the 2-methylphenyl ligand. No significant increase in chemical shift due to the electron withdrawing effect of the acyl group was recognised. A strong singlet at δ1.44 (relative intensity 18H) suggests the presence of two *tert*-butylimido groups. The ^{13}C-$\{^{1}H\}$ n.m.r. shows the six unique aromatic carbons of the 2-methylphenyl rings at δ125.6, 126.4, 129.4, 130.8, 135.5 and 138.1 and a low field peak at δ169.7, possibly due to the two acyl carbons. Peaks at δ28.9 and 29.6 represent the *tert*-butylmethyl and the 2-methyl carbons respectively. The peak at δ51.7 could possibly be assigned to the tertiary carbon on the *tert*-butylimido ligands, however recent work in these laboratories [55] on $(^{t}BuN)_3Re(aryl)$ compounds shows that the tertiary carbon lies in the range δ70-74. From n.m.r. integration and elemental analysis the ratio of acyl and imido groups is 1:1 and with no other aromatic group discernable from the ^{13}C n.m.r. we would postulate the structure as $(^{t}BuN)_2Re(C(O)C_6H_4\text{-}2\text{-}Me)_2$. The reaction, however, could not be repeated successfully, and it is possible that adventitious oxygen caused partial oxidation to $ReOR_4$ and then further reaction with the isocyanate led to the acyl product. However, no reaction occurred when *tert*-butylisocyanate was reacted with $ORe(2\text{-}MeC_6H_4)_4$.

The addition of silver tetrafluoroborate to the tetraaryl in acetonitrile turns the reaction mixture dark green with precipitation of silver metal. Dichloromethane addition, deposits more silver and a dark powder, which can be dissolved in acetonitrile to give dark blue/purple solutions. The purple solid gives ^{1}H n.m.r. similar to that of the starting material. Biphenyl and peaks for BF_3^+ and BF_2^+ appear in the mass spectrum. It would be interesting to assume that

the cation $(BF_4)[Re^V(2\text{-}MeC_6H_4)_4]$ is formed and the conductivity in acetonitrile falls in the specified range for an 1:1 electrolyte [56] (Λ_M = 135 Ω^{-1} cm^2 mol^{-1}).

The reaction of one equivalent of the free radical TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) with the tetraaryl at -78°C in diethyl ether yields the postulated dioxotris(2-methylphenyl)rhenium(VII) compound,after 24h. stirring, as a blue/green powder. The mass spectrum shows the parent ion, m/e 491 and subsequent losses of oxygen and aryl ligands. Peaks at m/e 401 (82%) and 399 (47%) are equivalent to ^{187}Re and $^{185}ReO_2R_2^+$ respectively; this formulation has only previously been observed with xylyl and mesityl ligands. The reaction of TEMPO to give an oxo compound has been observed by Jaitner *et al* [57] where photolysis of group VI hexacarbonyls (M=Mo,W) with the nitroxyl radical leads to the highly oxidised hydroxylamido compounds, $(TEMPO)_2MoO_2$ and $(TEMPO)_5W_3O_5$.

At the time of writing, the author has inconclusive data for the aforementioned compounds, however further studies are in progress.

(B) *cis*-Dioxo Species of Rhenium(V) and -(VI)

(i) Preparation and characterisation of $[(xylyl)_2ReO_2]_2Mg(thf)_2$

The interaction of either trimethylammonium per-rhenate or dirhenium heptoxide with seven equivalents of xylylmagnesium bromide per Re atom in thf gives diamagnetic air-sensitive, red/purple crystals of $[(xylyl)_2ReO_2]_2Mg(thf)_2$ (xylyl = 2,6-dimethylphenyl), which can be crystallised from diethyl ether. The crystallinity of the compound depends on solvation and further recrystallisation may lead to precipitation of a purple powder.

The compound is soluble in aromatic hydrocarbons and ethers but

decomposes rapidly in halogenated solvents.

The formation of a $(xylyl)_2ReO_2^-$ unit, as opposed to $(xylyl)_4ReO^-$ which might be expected by analogy with the rhenium oxo-alkyls [19a], may be a result of the steric demand of the xylyl group (see the case of substitution reactions on $M(mesityl)_nX_{5-n}$ [30], M = Nb or Ta, X = Cl or Br, n = 1-3) although the binding of four mesityls to rhenium can be obtained by the appropriate selection of starting material, *e.g.* $ReOCl_4$ to make $ReO(mes)_4$.

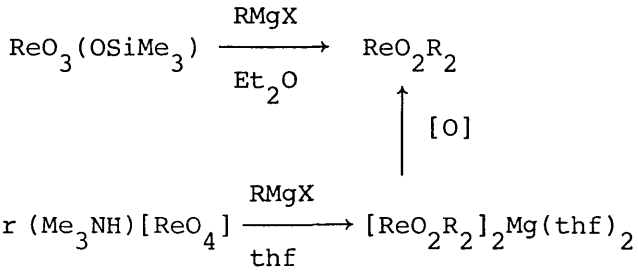
The i.r. spectrum contains peaks at 1025, 1005, 920, 900 and 860 cm^{-1} that can be assigned to skeletal vibrations of thf [58]. The Re=O stretches are masked by those stretches somewhat, although shoulders at 992 and 943 cm^{-1} could tentatively be assigned. Presumably the tetrahedral $(xylyl)_2ReO_2^-$ units are co-ordinated to Mg *via* one oxygen only, while the magnesium atom is solvated by two thf groups. A bridging Re-O stretch would therefore be expected at lower frequency, compared to the 975 and 930 cm^{-1} stretches of the "free" $ReO_2(xylyl)_2$ compound, and this stretch is probably obscured by the broad vibrations of the thf.

Unlike the analogous mesityl compound, the ^{13}C spectrum proved to be more useful than the ^1H n.m.r. At ambient temperatures the ^1H n.m.r. spectrum shows the usual doublet and triplet pattern for the aromatic protons at δ6.65 and 6.91 while the broad thf peaks can be seen at δ1.25 and 3.57. However, the *ortho*-methyl groups show complicated patterns - two sharp peaks (δ2.14 and 2.79) and a broad hump between δ2.6 - 3.2, possibly caused by restricted rotation about the $Re-C_\alpha$ bond and the non-equivalence of the *ortho*-methyls on the xylyl ligands. The $^{13}C-\{^1H\}$ n.m.r. shows six unique aromatic carbons at δ124.3, 125.3, 126.4, 130.2, 137.7 and 150.0, co-ordinated thf at δ25.3 and 68.8 and an extremely broad peak at δ29.6, presumably due to the non-equivalent

ortho-methyls.

(ii) Synthesis and structure of $ReO_2(xylyl)_2$

In thf the solvated magnesium complex is rapidly oxidised by dry oxygen or by addition of aqueous hydrogen peroxide to give bright red solutions from which the paramagnetic (Re^{VI}, d^1), deep red crystalline complex can be obtained in moderate yields. Higher yields are afforded from the reaction of xylyl Grignard and trimethylsilyl per-rhenate(VII) (scheme 1), the product being formed directly - the oxidation step is not required. The mesityl analogue can also be prepared in this way in higher yields. The expected product of this reaction $ReO_3(xylyl)$, however, proved elusive to isolate, although it can be seen in high percentage in the mass spectrum. Even with slow addition of xylyl or mesityl Grignard at low temperatures, the ReO_2R_2 compound was the major product.



Scheme 1

The i.r. spectrum of the compound shows two strong peaks at 975 and 930 cm^{-1} for the Re=O stretches of the *cis*-ReO_2 unit [19b,59], and like $ReO_2(mesityl)_2$, the xylyl compound shows high air and thermal stability in the solid state. However the complex slowly decomposes in solution over a period of several days on exposure to air, turning from bright red to pale yellow.

The structure of the molecule [55], which has crystallographic C_2 symmetry is shown in Figure 2.5 with selected bond lengths and angles in Table 2.4. The geometry of the molecule is realistically described as tetrahedral, although not unexpectedly the O-Re-O angle is enlarged due to repulsion between the electron density in the Re=O multiple bonds, and the C-Re-C angle reduced from the idealised value. The bonding of the xylyl ligand is not quite symmetrical, with Re-C-C angles differing by *ca.* 3°. This is probably due to the steric repulsion between the oxygen atoms and the C(28) methyl groups, since the angle Re-C(21)-C(26) is greater than Re-C(21)-C(22). Although the stability of the compound may be ascribed, in part, to the shielding effect of the four *ortho*-methyl groups, there are no unusually short Re----H contacts.

The formation of ReO_2R_2 compounds is quite unique among the known oxoorgano-rhenium species and to our knowledge is only one of a few examples of tetrahedral co-ordination around a Re^{VI} centre, other than $ReO_2(mesityl)_2$ [19b], the ion ReO_4^{2-} [60] and perhaps the recently claimed ReO_2Cl_2 [61]. The closest analogues are $MoO_2(mesityl)_2$ [53], OsO_2R_2 R = xylyl [62] and mesityl [19b], and a number of stabilised complexes, $MoO_2R_2(bipy)$ (R=Me [63], CH_2CMe_3 [64] or CH_2Ph [65], bipy = 2,2'-bipyridyl) although a supporting base was found indispensable for these alkyls.

The mass spectrum of $ReO_2(xylyl)_2$ shows both parent ions, m/e 429 and 427 and all subsequent losses of xylyl groups.

The electron spin resonance spectra of $ReO_2(xylyl)_2$ prepared under anaerobic conditions gave a simple spectra with a six-line hyperfine structure at 293K at *X*-band (g_{iso} = 1.967, A_{iso} = 0.0194 cm^{-1}) (see Figure 2.6). When the temperature of the solution was lowered, the spectrum gradually resolved into a complicated pattern (see Figure 2.7),

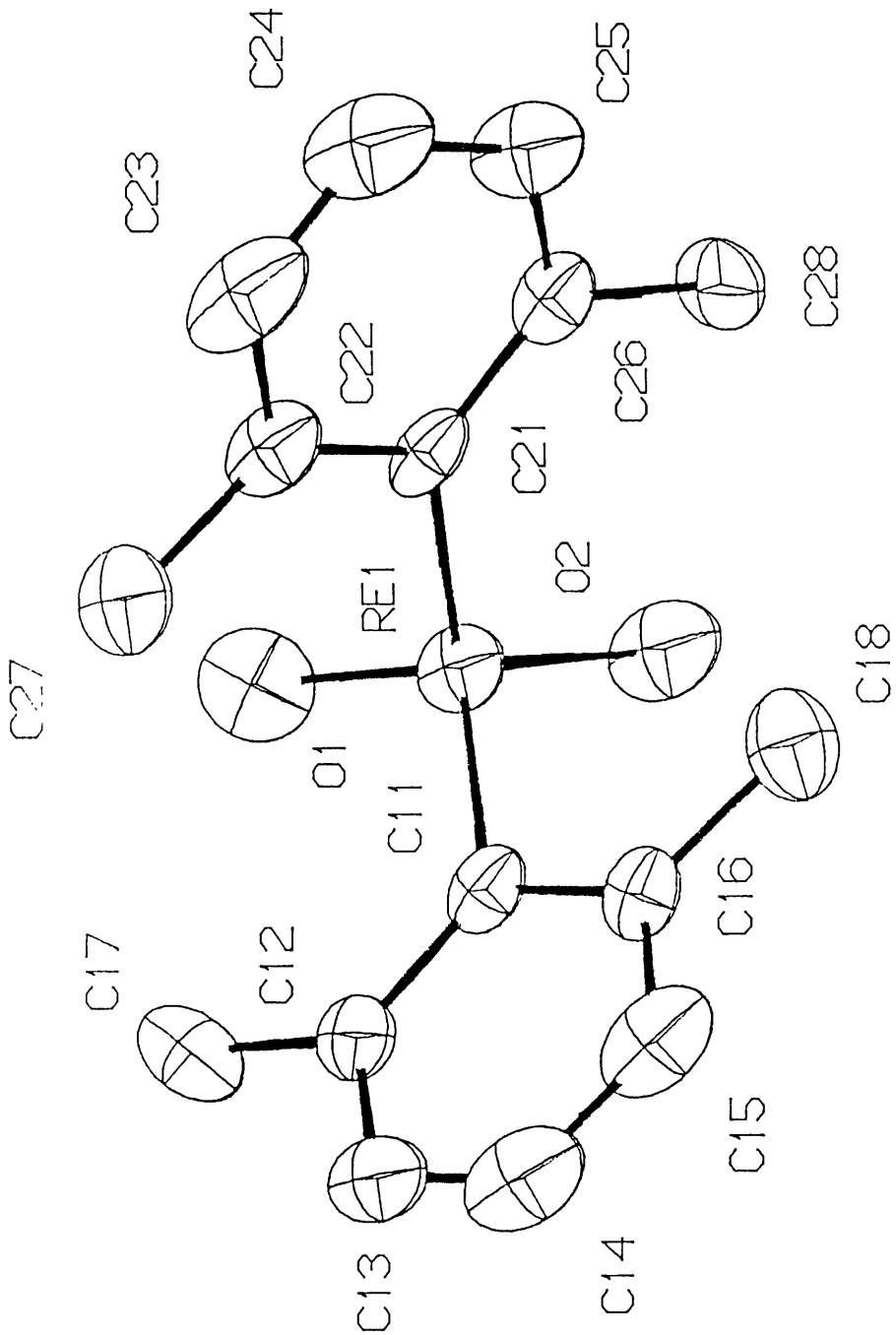


Figure 2.5: The molecular structure of $Re^{VI}O_2(xylyl)_2$.

Table 2.4: Selected bond lengths (Å) and angles (deg.) for $Re^{VI}O_2(xylyl)_2$.

Bond Lengths

Re-O(1)	1.690
Re-O(2)	1.667
Re-C(11)	2.068
Re-C(21)	2.075

Bond Angles

C(11)-Re-O(1)	110.17
C(11)-Re-C(21)	100.42
O(1)-Re-O(2)	121.47
O(2)-Re-C(11)	106.76
O(2)-Re-C(21)	109.29
O(1)-Re-C(21)	106.73
Re-C(21)-C(26)	122.08
Re-C(21)-C(22)	118.80
Re-C(11)-C(16)	118.70
Re-C(11)-C(12)	121.48

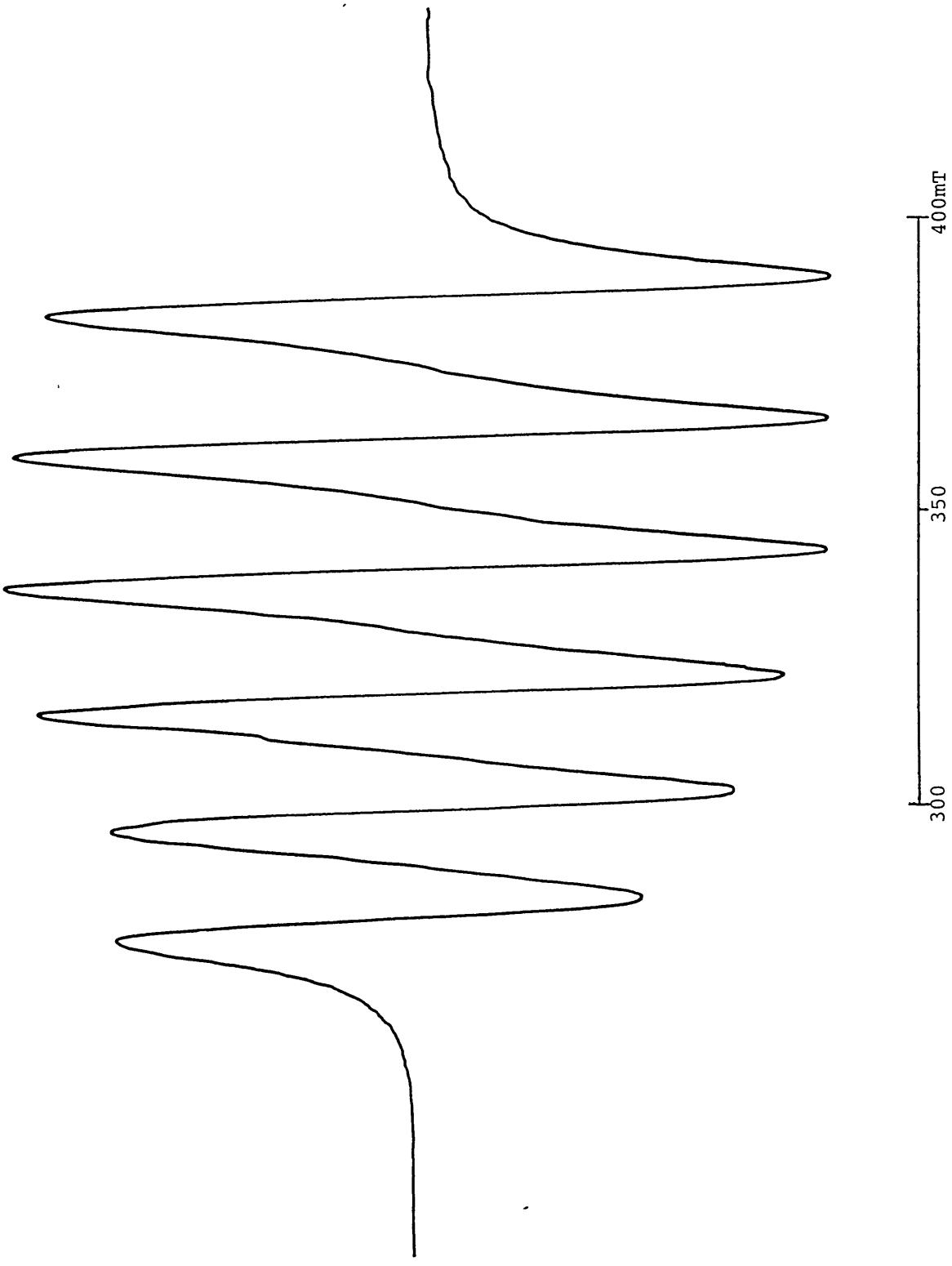


Figure 2.6: The E.S.R. spectra (*X*-band) of $ReO_2(xylyl)_2$ at 293K.

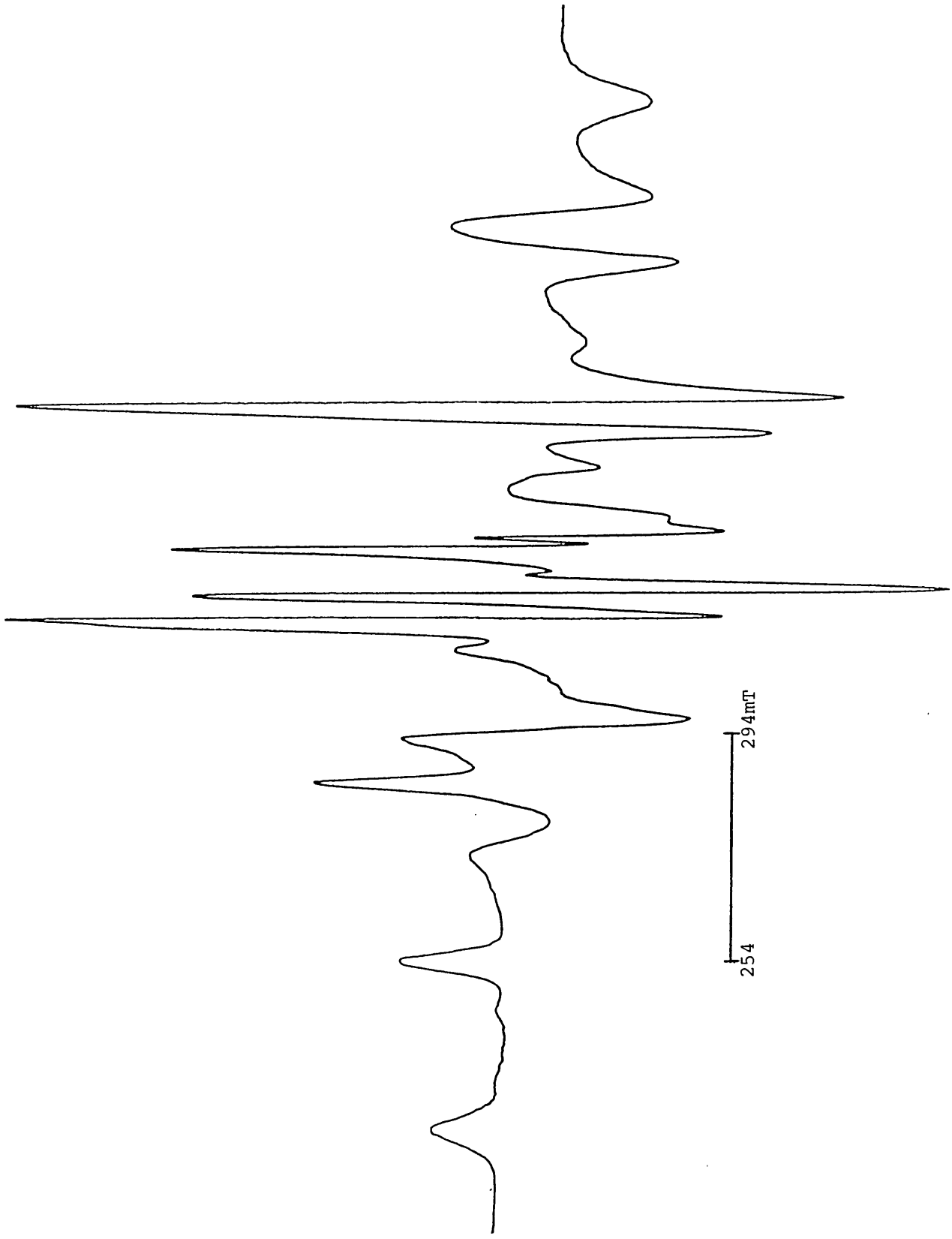


Figure 2.7: The E.S.R. spectra (*X*-band) of $ReO_2(xylyl)_2$ at 98K.

showing, at 98K, more than two sets of six rhenium hyperfine lines with unequal spacing. The *Q*-band spectrum showed that this pattern corresponds to a molecule with rhombic symmetry with the *z* and *x*-axis well apart, whereas the *y*-axis lies in between ($g_z > g_y > g_x$ and $A_z > A_x > A_y$). The parameters for the *z*-axis ($g_z = 2.094$, $A_z = 0.0337$) and the *x*-axis ($g_x = 1.865$, $A_x = 0.0244$) were derived directly from the experimental fields of the *Q*-band spectrum whereas parameters for the *y*-axis ($g_y = 1.943$, $A_y = -4 \times 10^{-4}$) were calculated from the isotropic and anisotropic values by using the equations

$$g_y = 3g_{iso} - g_z - g_x$$

and

$$A_y = 3A_{iso} - A_z - A_x \ .$$

(C) Trisoxorhenium(VII) aryl compounds

(i) Synthesis and characterisation of ReO_3(mesityl)

The reaction of three equivalents of Al(mesityl)$_3$thf with $O_3Re(OSiMe_3)$ in hexane at -78°C gave the title compound plus small amounts of ReO_2(mesityl)$_2$. This can be demonstrated by analysing the i.r. and mass spectra. The i.r. shows the mesityl ligand vibrations plus two new peaks in the R=O stretching range at 1000 and 955 cm^{-1}. Very small peaks at 975 and 930 cm^{-1} indicate the presence of ReO_2(mesityl)$_2$ in small quantity. A new peak at 870 cm^{-1} is also found as well as a very strong band at 595 cm^{-1}. The mass spectrum shows the parent ions at m/e 354 and 342 for $^{187}ReO_3$(mesityl) and $^{185}ReO_3$(mesityl) respectively as well as the fragmentation peaks of the molecule. Higher mass peaks due to ReO_2(mesityl)$_2$ are also present.

The ^{1}H n.m.r. spectrum shows two sharp singlets at δ2.05 and 2.55 (relative intensity 1:2) due to the *para* and *ortho*-methyls respectively. A peak at δ6.95 can be readily assigned to the aromatic protons. The $^{13}C-\{^{1}H\}$ n.m.r. spectrum shows the *ortho*-methyl groups at δ21.1, the *para*-methyl at δ27.8 and of the aromatic carbons, only three can be seen at δ148.0, 145.8 and 137.6, the other three carbons being obscured by benzene-d_6 solvent.

The reaction of $O_3Re(OSiMe_3)$ with xylyl or mesityl Grignard reagents led predominantly to the ReO_2R_2 product in good yields, although very small amounts of O_3ReR were formed. Slow addition of the Grignard failed to inhibit the reduction of rhenium from Re^{VII} to Re^{VI}, although rhenium(VII) aryl compounds are now known [55], *e.g.* $(^{t}BuN)_3ReR$ where R = 2-methylphenyl, xylyl and mesityl.

Less bulky ligands provided more complicated reaction mixtures. From the mass spectrum, $O_3Re(2\text{-}MeC_6H_4)_4$ and the previously unknown $ReO_2(2\text{-}MeC_6H_4)_2$ can be observed. Both compounds proved difficult to manipulate, as repeated recrystallisation and the action of reduced pressure caused some decomposition, and elemental analysis showed the presence of Mg.

Further work with the less reducing trisarylaluminium compounds may produce the desired compounds.

It is interesting to note that the alkylation of $O_3Re(OSiMe_3)$ with trimethylaluminium led to the isolation of $Re_2O_3Me_6$ [19a]. The only previously reported organometallic trisoxorhenium compound, ReO_3(methyl), was prepared by air oxidation of either $ReOMe_4$ or *cis*-ReO_2Me_3 [49]. This air-stable, water resistant compound exhibited peaks in the i.r. at 1000 and 966 cm^{-1} assigned to ReO_3 symmetric and antisymmetric stretches respectively, in good agreement with O_3Re(mesityl).

Experimental

E.S.R.: Varian E-9 (*X*-band) and Bruker ER 200D-SRC (*Q*-band). Re_2O_7 [66], $O_3Re(OSiMe_3)$ [67] and $ReCl_4(thf)_2$ [68] were prepared as before. Trimethylammonium per-rhenate was prepared by dissolving rhenium in 30% H_2O_2 and neutralising the solution with Me_3N; the salt was crystallised from ethanol-water.

Other details on the spectrometers used and of the experimental procedures are given in the experimental section of Chapter 1.

2.1) Tetrakis(2-methylphenyl)rhenium(IV)

To a stirred suspension of $ReCl_4(thf)_2$ (0.54 g, 1.14 mmol) in thf (30 cm^3) at -78°C was added 2-methylphenylmagnesium bromide (2.6 cm^3 of a 1.0 mol dm^{-3} solution in Et_2O, 2.60 mmol) and the mixture warmed to room temperature and stirred overnight.

The volatile material was removed under reduced pressure and the residue extracted with hexane (4 × 30 cm^3). Concentration of the filtered extracts to *ca.* 30 cm^3 and cooling overnight (-20°C) affords dark red crystals.

Yield: 0.18 g, 29%.

I.r.: 3050m, 1564w, 1440m, 1281w, 1247w, 1190w, 1110m, 1052w, 1028m and 740s.

Mass Spectrum: m/e 551 (18%) $^{187}Re(2\text{-}MeC_6H_4)_4^+$, 549 (11%) $^{185}Re(2\text{-}MeC_6H_4)_4^+$, 459 (24%) $^{187}Re(2\text{-}MeC_6H_4)_3^+$, 457 (21%) $^{185}Re(2\text{-}MeC_6H_4)_3^+$, 369 (3%) $^{187}Re(2\text{-}MeC_6H_4)_2^+$, 367 (8%) $^{185}Re(2\text{-}MeC_6H_4)_2^+$, 91 (100%)$C_7H_7^+$.

N.m.r. ^1H: 2.39 (3H, s, 2-Me), 7.20 (2H, m, C_6H_4) and 7.28 (2 H, m, C_6H_4);

^{13}C: 26.5 (*s*, 2-Me), and 125.3, 127.1, 128.2, 129.0, 129.7 and 141.6 (*s*, C_6H_4).

2.2) Oxotetrakis(2-methylphenyl)rhenium(VI)

2-Methylphenylmagnesium bromide (2.5 cm^3 of a 1.0 mol dm^{-3} solution in Et_2O, 2.54 mmol) was added to $ReCl_4(thf)_2$ (0.5 g, 1.06 mmol) in thf (35 cm^3) and the mixture warmed to room temperature and stirred for 6h. The volatile materials were removed and the residue extracted with hexane (3 × 25 cm^3) in air, the blue/green filtrate reduced to *ca.* 15 cm^3 and cooled to give green/blue needles.

Yield: 0.21 g, 35%.

I.r.: ν(Re=O), 992s (982sh). Other: 3040m, 1610m, 1280m, 1250m, 1190s, 1155m, 1110s, 1050m, 1030w, 1010w, 940w, 860m, 785m, 745(sh), 740s, 705m, 640w, 590w, 490w, 440s, 415m.

Mass Spectrum: m/e 475 (5%)$ReOR_3^+$, 385 (99%) $^{187}ReOR_2^+$, 383 (100%) $^{185}ReOR_2^+$, 369 (5%) $^{187}ReR_2^+$, 367 (6%) $^{185}ReR_2^+$, 294 (31%) $^{187}ReOR^+$, 292 (30%) $^{185}ReOR^+$, 278 (5%) $^{187}ReR^+$, 91 (33%) $C_7H_7^+$.

E.s.r. (in cm^{-1}): g_z = 2.083, g_x = 1.932, A_z = 0.0320. A_x = 0.0274.

2.3) Nitrosobis(2-methylphenyl)rhenium(III)

$Re(2\text{-}MeC_6H_4)_4$ (0.21g, 0.38 mmol) was dissolved in hexane (35 cm^3) at -78°C and purified NO (1 atmosphere) was added and stirred for 1 minute. The bright red powder was collected and recrystallised from diethyl ether (25 cm^3) to yield red semi-crystalline solid.

Yield: 0.12g, 79%.

I.r.: 1642m, 1574m, 1310m, 1265m, 1155w, 1110m, 1018w, 831w, 762m, 741s, 642w, 630w, 615w, 460w.

Mass Spectrum: m/e 182 (38%) R_2^+, 167 (29%) $R_2\text{-}Me^+$, 152 (8%) $R_2\text{-}2Me^+$, 91 (100%) $C_7H_7^+$.

N.m.r. ^1H: 2.00 (3H, s, 2-Me), 7.01 (2H, m, C_6H_4) and 7.22 (2 H, m, C_6H_4).

2.4) Chlorobis(2-methylphenyl)rhenium(III)

$Re(2\text{-}MeC_6H_4)_4$ (0.15 g, 0.27 mmol) was dissolved in hexane (30 cm^3) at -78°C and chlorine (1 atmosphere) was added and stirred for 30 seconds. The volatile materials were removed and the bright red powder was washed with ether (2 × 20 cm^3) and dried *in vacuo*.

Yield: 0.06 g, 55%.

I.r.: 1565m, 1549w, 1305m, 1280s, 1260w, 1191s, 1160m, 1110br, 1025br, 860w, 792w, 741s, 605w, 508w, 470w.

Mass Spectrum: m/e 182 (47%) R_2^+, 167 (49%) $R_2\text{-}Me^+$, 152 (13%) $R_2\text{-}2Me^+$, 91 (100%) $C_7H_7^+$.

N.m.r. ^1H: 2.00 (3H, s, 2-Me), 7.04 (2H, m, C_6H_4) and 7.18 (2H, m, C_6H_4).

2.5) "Di(*tert*-butylimido)di(2-methylphenylacyl)rhenium(VI)"

$Re(2\text{-}MeC_6H_4)_4$ (0.12 g, 0.22 mmol) was dissolved in hexane (50 cm^3) at -78°C and *tert*-butylisocyanate (0.09 g, 0.88 mmol) was added in hexane (20 cm^3) and the mixture was warmed to room temperature and refluxed for 24h. The green solution was filtered, concentrated to *ca.* 40 cm^3 and cooled to -20°C overnight. The green solid was collected and dried *in vacuo*.

Yield: 0.082 g, 66%.

I.r.: 1642s, 1571m, 1405(sh), 1370m, 1298m, 1262s, 1218(br), 1100(br), 1018(br), 975m, 935(sh), 901s, 800s, 740m, 660w, 460w.

Mass Spectrum: m/e 376 (2%) $(^tBuN)_2Re^+$, 305 (6%) $(^tBuN)Re(COC_7H_7)^+$, 257 (3%) $(^tBuN)Re^+$, 238 (54%) $C_7H_7CO\text{-}COC_7H_7^+$, 208 (10%) $C_6H_4CO\text{-}COC_6H_4^+$, 119 (100%) $C_7H_7CO^+$, 91 (53%) $C_7H_7^+$, 71 (2%) $^tBuN^+$, 57 (64%) $C_4H_9^+$.

N.m.r. ^{1}H: 1.44 (18H, s, Me_3CN), 2.40 (6H, s, 2-*Me*), 7.22 (4H, m, C_6H_4), 7.31 (4H, m, C_6H_4).

^{13}C: 28.9 (*s*, Me_3CN), 29.6 (*s*, 2-Me), 51.7 (*s*,$NCMe_3$), 125.6, 126.4, 129.4, 130.8, 135.5 and 138.1 (*s*, C_6H_4) and 169.7 (*s*, COC_7H_7).

2.6) Tetrakis(2-methylphenyl)rhenium(V)Tetrafluoroborate

$AgBF_4$ (0.111 g, 0.58 mmol) was dissolved in acetonitrile (20 cm^3) and added to $Re(2\text{-}MeC_6H_4)_4$ (0.32 g, 0.58 mmol) in acetonitrile (20 cm^3) and stirred for 24h. The green solution was filtered and concentrated to dryness under reduced pressure. Dichloromethane (10 cm^3) was added, and the resulting red solution filtered away. The purple powder was dissolved in acetonitrile (5 cm^3), filtered and concentrated to dryness to give purple micro-crystalline solid.

Yield: 0.17 g, 46%.

I.r.: 1281m, 1100(br), 1050(sh), 1019(sh), 910m, 841m, 760m, 521m, 469m.

Mass Spectrum: m/e 182 (35%) R_2^+, 167 (4%) $R_2\text{-}Me^+$, 91 (6%) $C_7H_7^+$, 68 (5%) BF_3^+, 49 (100%) BF_2^+.

N.m.r. ^{1}H: 2.01 (3H, s, 2-Me), 7.05 (2H, m, C_6H_4) and 7.26 (2H, m, C_6H_4).

Conductivity (MeCN): $\Lambda_M = 135\ ohm^{-1}cm^2mol^{-1}$.

2.7) Bis(tetrahydrofuran)magnesiumbis[dioxodixylylrhenate(V)]

To a cooled (-78°C) suspension of Re_2O_7 (1.30 g, 2.68 mmol) in thf (45 cm^3) was added xylylmagnesium bromide (31.3 cm^3 of a 1.20 mol dm^{-3} solution in Et_2O, 37.6 mmol). The mixture was allowed to warm slowly and was held at room temperature for *ca.* 1h. The resulting red/purple solution was evaporated and the residue extracted with diethyl ether (3 × 20 cm^3), filtered and concentrated to

ca. 40 cm^3 to afford,on cooling to -20°C,red/purple crystals.

Yield: 0.48 g, 18%.

I.r.: 1572m, 1555w, 1348w, 1299w, 1250w, 1215m, 1180w, 1160w, 1120w, 1075s, 1025(vbrs), 1005(sh), 992(sh), 943(sh), 920s, 900(sh), 860s, 822(sh), 760s, 709m, 678m, 551m, 520w, 471m, 440w.

N.m.r. ^1H: δ6.91 (8 H, d, C_6H_3), 6.65 (4 H, t, C_6H_3), 3.57 (8 H, m, α-CH_2(thf)), 2.6-3.2 and 2.14 (24 H, broad, *o*-CH_3), 1.25 (8 H, m, β-CH_2(thf)).

^{13}C-{^1H}: δ25.3 (s, β-CH_2 thf), 29.6 (brs, *o*-CH_3), 68.8 (s, α-CH_2 thf), 124.3, 125.3, 126.4, 130.2, 137.7 and 150.0 (s, C_6H_3).

2.8) Dioxodixylylrhenium(VI)

To a stirred solution of $O_3Re(OSiMe_3)$ (0.85 g, 2.64 mmol) in thf (30 cm^3) was added xylylmagnesium bromide (4.4 cm^3 of a 1.20 mol dm^{-3} solution in Et_2O, 5.28 mmol) and the solution was warmed to room temperature and stirred for 2h. The resulting red solution was evaporated and the residues were extracted into diethyl ether (3 × 25 cm^3), filtered and concentrated to *ca.* 45 cm^3 and cooled at -20°C overnight to yield dark red crystals.

Yield: 0.71g, 63%.

I.r.: 3000m, 1566m, 1230m, 1165m, 1115w, 1026s, 975s, 930s, 855w, 770s, 705w.

Mass Spectrum: m/e 429 (51%) $^{187}ReO_2R_2^+$, 427 (35%) $^{185}ReO_2R_2^+$, 324 (7%) $^{187}ReO_2R^+$, 332 (16%) $^{185}ReO_2R^+$, 308 (12%) $^{187}ReOR^+$, 306 (4%) $^{185}ReOR^+$, 105 (100%) R^+, 91 (73%) $C_7H_7^+$.

E.s.r.: g_{iso} = 1.967, A_{iso} = 0.0194, g_z = 2.0937, A_z = 0.0377, g_y = 1.943, A_y = -4.0×10^{-4}, g_x = 1.865, A_x = 0.0244, energies in cm^{-1}.

2.9) Dioxodimesitylrhenium(VI)

The title compound can be made in high yields (60-70%) by following the experimental procedure in 2.8 and substituting mesitylmagnesium bromide for the xylyl Grignard.

I.r.: ν(Re=O) 972s, 930s. Other: 3000m, 1580s, 1278s, 1260(sh), 1030m.br, 1000w, 952w, 915w, 850s, 700m, 595w, 550m, 545(sh), 360w.

Mass Spectrum: m/e 457 (61%) $^{187}ReO_2R_2^+$, 455 (37%) $^{185}ReO_2R_2^+$, 338 (41%) $^{187}ReO_2R^+$, 336 (26%) $^{185}ReO_2R^+$, 238 (6%) R_2^+, 119 (100%) R^+, 91 (23%) $C_7H_7^+$.

E.s.r.: g_{iso} = 1.971, A_{iso} = 0.0187, g_z = 2.094, A_z = 0.0355, g_y = 1.954, A_y = -0.0036, g_x = 1.865, A_x = 0.0242, energies in cm^{-1}.

2.10) Trisoxomesitylrhenium(VII)

To a hexane (20 cm^3) solution of $O_3Re(OSiMe_3)$ (0.5 g, 1.55 mmol) was added $Al(mesityl)_3thf$ (2.11 g, 4.65 mmol) in hexane (40 cm^3) and the solution warmed to room temperature. The red solution was recooled at -20°C and degassed water (5 cm^3) was added. The mixture was warmed until the ice melted then immediately cooled to -20°C and the mixture filtered. The red solution was concentrated to *ca.* 20 cm^3 and cooled to -20°C overnight to give red crystals.

Yield: 0.25g, 46%.

Small amounts of $ReO_2(mesityl)_2$ also co-crystallise with the title compound.

I.r.: 1588w, 1281s, 1029m, 1000s, 955s, 870s, 845s, 695s, 595s, 581w, 551m.

Mass Spectrum: m/e 354 (100%) $^{187}ReO_3R^+$, 352 (66%) $^{185}ReO_3R^+$, 336 (25%) $^{185}ReO_2R^+$, 322 (17%) $^{187}ReOR^+$, 320 (3%) $^{185}ReOR^+$, 306 (17%) $^{187}ReR^+$, 304 (9%) $^{185}ReR^+$, 119 (77%) R^+, 105 (33%) $R\text{-}Me^+$, 91 (40%) $R\text{-}2Me^+(C_7H_7^+)$.

N.m.r. ^{1}H: δ2.05 (3 H, s, *p*-CH_3), 2.55 (6 H, s, *o*-CH_3), 6.95 (2 H, s, C_6H_2);

$^{13}C-\{^{1}H\}$: 21.1 (s, *o*-CH_3), 27.8 (s, *p*-CH_3), and 137.6, 145.8 and 148.0 (s, C_6H_2).

CHAPTER 3

HOMOLEPTIC ARYL AND OXO-ARYLS OF OSMIUM

HOMOLEPTIC ARYL AND OXO-ARYLS OF OSMIUM

Introduction

Among the third row transition metals, the chemistry of high oxidation state organoosmium compounds has only sporadically been explored. One of the reasons for this is that osmium tetraoxide is a powerful oxidant and a very expensive material, so it is not surprising that it has only moderately been used for alkylations, unlike the per-rhenates (see Chapter 2).

Few high oxidation state organoosmium complexes have been reported. Square pyramidal $OsO(CH_2SiMe_3)_4$[20] and a series of nitridoosmium compounds[69] have been prepared directly and indirectly respectively, from OsO_4. An osmium(VIII) alkyl complex[70] has also been proposed as an intermediate in the oxidation of olefins by OsO_4. Among Os^{IV}, d^4 systems, $OsMe_4(PPh_3)_2$[20] has been prepared from $OsCl_6^{2-}$ and MeMgI. Very recent work in these laboratories includes the synthesis and X-ray characterisation of both homoleptic tetraalkyl and tetraaryl osmium(IV) compounds, *e.g.* Os(cyclohexyl)$_4$[18], Os(2-methylphenyl)$_4$[18] and Os(phenyl)$_4$[18b] as well as $Os^{VI}O_2$(mesityl)$_2$[19b], the first osmium(VI) oxo-aryl compound to be isolated. The compound $Os_2(\eta^3\text{-}C_3H_5)_2(CH_2CMe_3)_4$[17], which contains an unsupported triple metal-metal bond has also been prepared from the partially alkylated acetate dimer, $Os_2(\mu\text{-}O_2CMe)_2R_4$, where R = CH_2CMe_3 in this case or CH_2SiMe_3.

The general route taken in this work using commercially available oxides, oxoanions and metal halides has been continued; osmium tetraoxide is used here in a number of alkylation reactions. Robust aryls were preferred over alkyls both for their resistance to instant oxidation and the protection offered to the compounds

formed towards thermal or oxidative decomposition, in order to overcome the problem of the strong oxidising capacity of OsO_4.

In this chapter, further investigation of non-oxo homoleptic aryls is continued, including the electrophilic substitution reactions of Os(2-methylphenyl)$_4$. The isolation of the second osmium(VI) oxo-aryl compound is also reported. Properties and analytical data for the new compounds are collected in Table 3.1.

Results and Discussion

(A) Tetraaryls of osmium(IV)

(i) Preparation and characterisation of Os(4-^{t}Butylphenyl)$_4$

The interaction of osmium tetraoxide with seven equivalents of the aryl Grignard in thf yields a deep red solution from which the title compound can be isolated in low yield. The diamagnetic compound is very air sensitive and decomposition is evident after several days even in hexane or toluene solutions, to yield black intractable materials (presumably lower oxidation state osmium aryl complexes), and the bis(butylphenyl) compound. Interestingly, the bis(butylphenyl) compound is formed on melting the solid, subliming up the melting point tube as white crystals (m.p. 129°C [71]. Decomposition in the solid state is also observed, making correct elemental analyses difficult to obtain. In contrast, the Os(phenyl)$_4$ compound is stable at room temperature in the solid state, and X-ray diffraction studies reveal tetrahedral geometry around the osmium centre.

The ^{1}H n.m.r. spectrum of the ^{t}butylphenyl compound is quite simple, comprising a sharp singlet at δ1.41 assigned to the tertiary butyl group and a quartet at δ7.54 with the familiar unsymmetrical

Table 3.1: Properties and Analytical Data for Osmium Aryl Compounds

Compound	Colour	m.p.(°C)	Analysis (%) [a]	
			C	O
$Os(4\text{-}^{t}BuC_6H_4)_4$	red	106-108	67.0 (66.5)	
$Os(2\text{-}MeC_6H_4)_3(2\text{-}Me\text{-}4\text{-}COMeC_6H_3)$	red	153-154	60.0 (60.4)	2.4 (2.7)
$OsO_2(2,6\text{-}Me_2C_6H_3)_2$	green	144	44.8 (44.4)	7.2 (7.4)

a) Found (required), no hydrogen analysis possible in the presence of Os.

p-disubstitution pattern associated with 1,4-disubstituted phenyl rings. The $^{13}C-\{^{1}H\}$ spectrum shows the methyl carbons at δ31.4 and the tertiary carbon at δ34.5; all four unique aromatic carbon atoms can be seen at δ125.6, 126.7, 138.3 and 150.0. A modulated spin echo experiment shows that as expected only three carbons are not attached to any hydrogen atoms, confirming δ34.5 as the tertiary carbon atom and the peaks at δ138.3 and 150.0, probably due to the carbon atoms bonded to the *tert*-butyl group and the osmium centre respectively.

Due to the unstable nature of the compound no high mass peaks could be seen in the mass spectrum, even at low eV. However OsR_2^+ (m/e 456, 1%) is observed, as well as the bisaryl compound and its subsequent fragmentation pathway.

The formation of OsR_4 compounds from the reduction of OsO_4 is not surprising, as even thionyl chloride can easily reduce osmium tetraoxide to a mixture of $OsOCl_4$ and $OsCl_4$[72]. However, this group of osmium(IV) tetraalkyl or tetraaryl compounds are the first examples of tetrahedrally coordinated organoosmium(IV), d^4 species (only octahedral and distorted octahedral geometries have been observed previously) and are consistent with a stable e^4 (low spin) electronic configuration.

(ii) <u>Synthesis and characterisation of tris(2-methylphenyl)(2-methyl-4-acetylphenyl)osmium(IV)</u>

Tetrakis(2-methylphenyl)osmium(IV) was made in these laboratories in 1986 from the reaction of OsO_4 and *o*-tolylmagnesium bromide in moderate yields. The compound was found to be remarkably inert to reactions with small gases (*e.g.* NO, CO, CO_2, O_2 and H_2) and could be refluxed in acetic acid for 2-3 days without decomposition. It therefore made an ideal starting material for more vigorous

reaction chemistry.

The Friedel-Crafts acylation reaction, in which the entering electrophile is an acyl group, RCO, derived from a carboxylic anhydride was successfully undertaken.

The reaction of $Os(2\text{-}MeC_6H_4)_4$ with four equivalents of acetic anhydride and 8.8 equivalents of aluminium trichloride in dichloromethane at -78°C was warmed slowly to room temperature. The reaction can be followed by thin layer chromatography, although prolonged stirring (3 days) or gentle refluxing of the mixture still gave four different products. After extraction into diethyl ether, repeated passage of the mixture through a Kieselgel column gave unreacted starting material (1st fraction) and three different products, only one of which could be identified. The second fraction from the column can be crystallised to yield red crystals of the title compound in low yield. It shows a characteristic acyl stretch at 1677 cm^{-1} in the i.r. spectrum, slightly lower than the peak associated with *m*-methylacetophenone, $\nu(C = O) = 1685\ cm^{-1}$ [73], and the aromatic C=C vibration appears at 1575 cm^{-1}.

The ^1H n.m.r. spectrum is shown in Figure 3.1, and the tabulated data is collected in Table 3.2 for both ^1H and ^{13}C n.m.r.. For convenience in the following discussion, we have designated the acylated ring hydrogens with a prime, *i.e.* the hydrogen between the methyl and the acyl functions is called 3'-H. The ^1H n.m.r. spectrum shows three sharp singlets at δ2.32, 2.42 and 2.53 (intensities 9:3:3) due to the methyl protons on the *o*-tolyl rings, the *o*-methyl on the acylated ring and the acyl methyl respectively. Figure 3.2 shows the 2-dimensional COSY spectrum of the complicated aromatic region and seven isolated peak patterns are observed, four with an integral of three and three peaks with an integral of one. The triplet at δ5.98

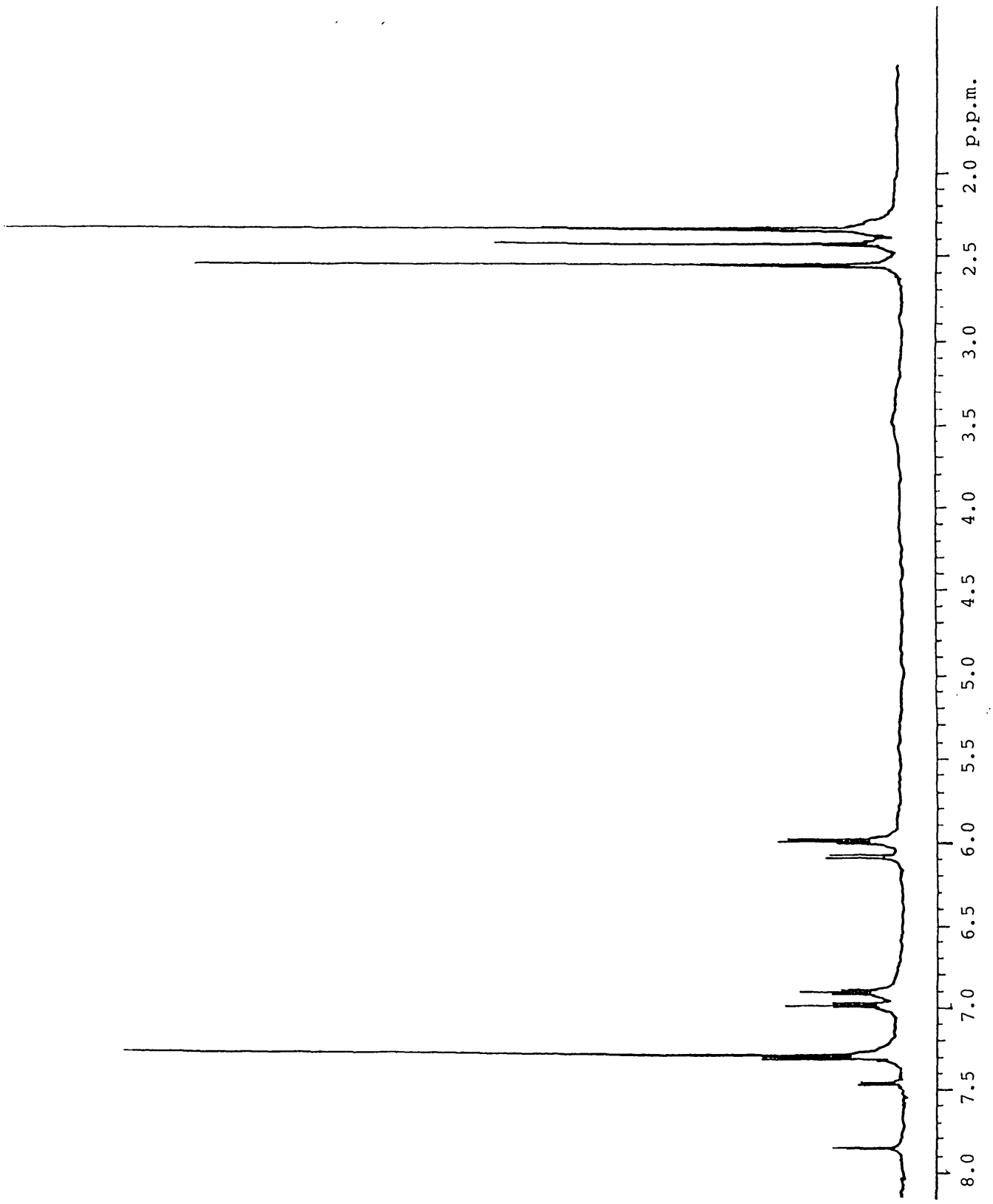


Figure 3.1: The ^{1}H n.m.r. spectrum of $Os(2\text{-}MeC_6H_4)_3(2\text{-}Me\text{-}4\text{-}COMe\text{-}C_6H_3)$.

Table 3.2: ^{1}H and $^{13}C-\{^{1}H\}$ n.m.r. Data for $Os(2\text{-}MeC_6H_4)_3(2\text{-}Me\text{-}4\text{-}COMeC_6H_3)$[a].

^{1}H	Assignment	$^{13}C-\{^{1}H\}$[b]
2.32s (9)	$2\text{-}CH_3C_6H_4$	26.5
2.42s (3)	$2'\text{-}CH_3\text{-}4\text{-}COCH_3\text{-}C_6H_3$	29.6
2.53s (3)	$2'\text{-}CH_3\text{-}4\text{-}COCH_3\text{-}C_6H_3$	29.7
5.98t (3)	6-H	124.4
6.07d (1)	5'-H	125.1
6.89m (3)	5-H	127.6
6.97m (3)	4-H	127.7
7.27m (3)	3-H	129.4
7.44dd (1)	6'-H	130.7
7.84d (1)	3'-H	133.0
		133.2
		133.4
		139.0
		139.2
		168.5
		198.0

(a) Referenced to $SiMe_4$ at δ0.00 p.p.m., in $CDCl_3$; relative intensities ( ); prime (') indicates functions on acylated ring.

(b) See Figure 3.3 for a guide to identifying peaks.

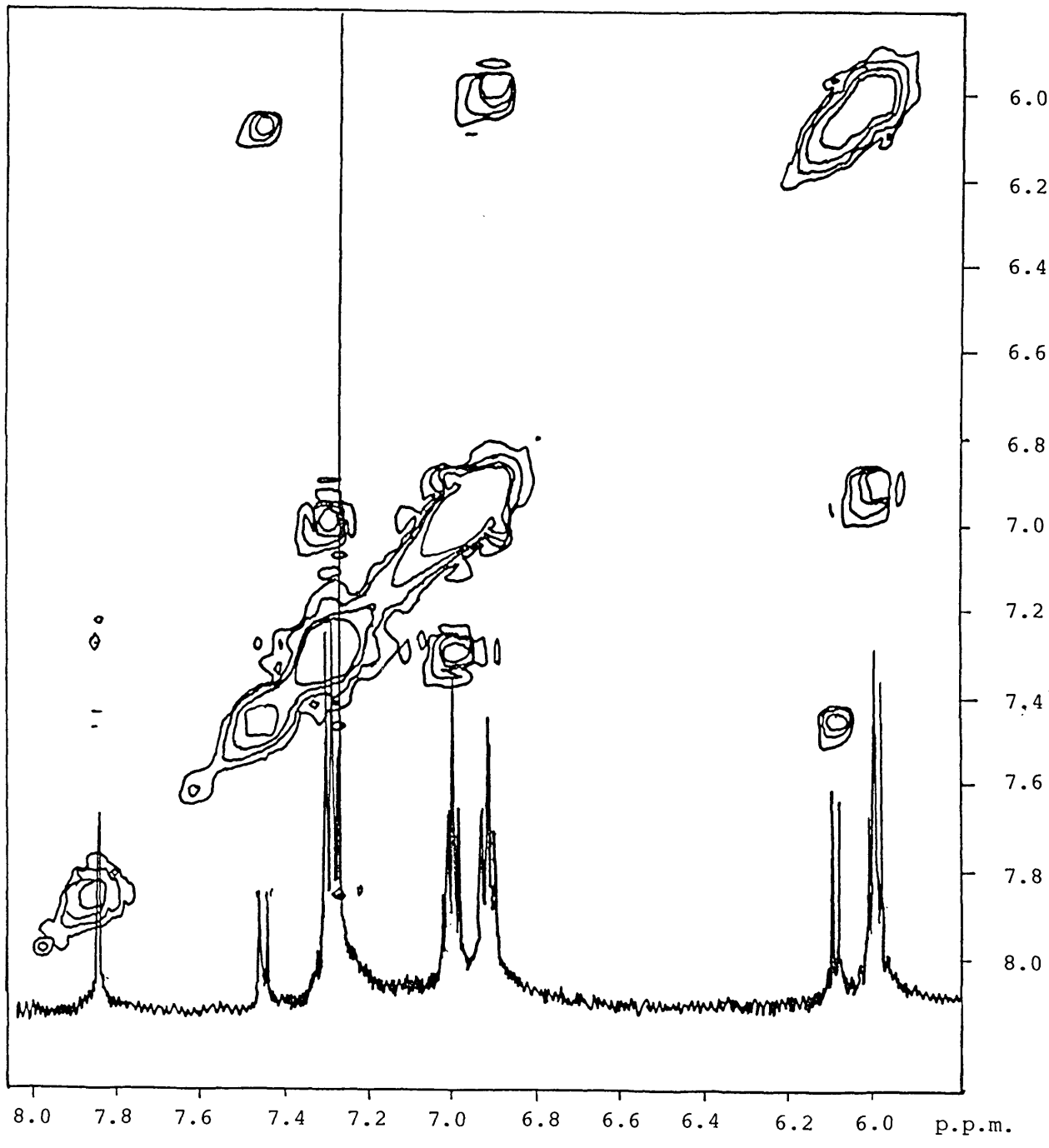


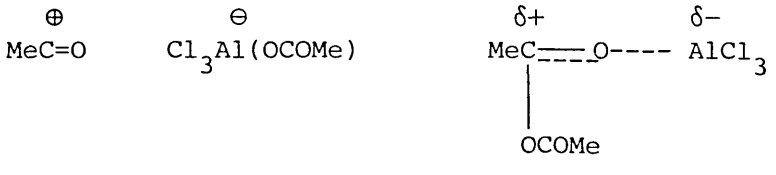
Figure 3.2: The 2-D COSY ^{1}H n.m.r. of $Os(2\text{-}Me\text{-}C_6H_4)_3(2\text{-}Me\text{-}4\text{-}COMe\text{-}C_6H_3)$.

(intensity 3) can be ascribed to the 6-hydrogen on the three *ortho*-tolyl rings. Multiplets at δ6.89, 6.97 and 7.27 (all intensity 3) are due to the 5-H, 4-H and 3-H on the three *ortho*-tolyl rings respectively. From the complete 2-D n.m.r. (δ0-10), a weak coupling between 3-H and the 2-methyl protons is observed. A similar weak 2-D coupling is seen between the 3'-H and the 2'-methyl protons on the acylated ring. The 3'-H appears as a doublet at δ7.84 ($J_{3'-6'}$ = 1.9Hz). If the acyl group was in the 5'-position, the 3'-H would be split into a doublet of doublets, hence the position of the acyl group in the 4'-position is confirmed. The 6'-H is split into a doublet of doublets at δ7.45 ($J_{3'-6'}$ = 1.9Hz, $J_{5'-6'}$ = 10.3Hz) and the 5'-H is split into a doublet at δ6.07 ($J_{5'-6'}$ = 10.3Hz) as expected.

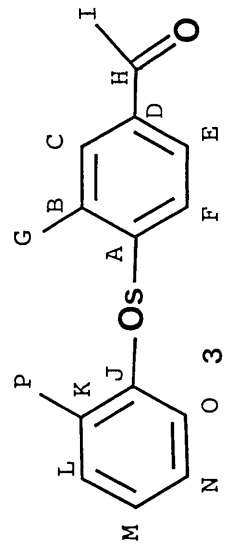
The $^{13}C-\{^{1}H\}$ n.m.r. spectrum can be seen in Figure 3.3 along with a rough guide for identifying the peaks.

The mass spectrum shows the acyl ligand m/e 133, 16% and some higher mass peaks.

Although the methyl group on the *ortho*-tolyl rings is *ortho, para*-directing, it would appear, as the acyl group has been directed onto the 4-position (*meta* to methyl) that either the osmium has the greater *ortho, para*-directing ability or that steric factors are involved in the substitution. This concerns the general dilemma of whether the effective electrophile is the acylium ion (I) or a polarised complex (II) [74]:



(I) (II)



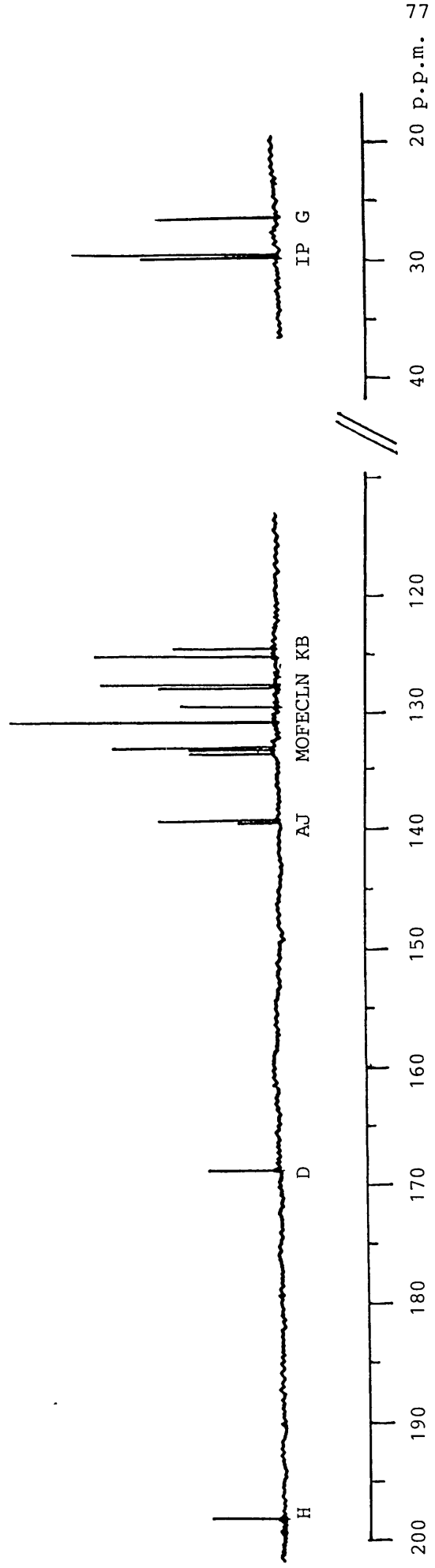


Figure 3.3: The $^{13}C-\{^{1}H\}$ n.m.r. $Os(2\text{-}MeC_6H_4)_3(2\text{-}Me\text{-}4\text{-}COMeC_6H_3)$.

Although acylium ions have been detected in the liquid complex between MeCOCl and $AlCl_3$ by infrared spectroscopy, with the bulky acetic anhydride there must be a high probability that the polarised complex acts as the electrophile, and therefore we believe that steric effects predominate. There can be little doubt that poly-acylation does not take place, as the product ketone is much less reactive than the original phenyl ring. It is interesting to speculate therefore that the other two unidentified products could be $Os(2\text{-}MeC_6H_4)_2(2\text{-}Me\text{-}4\text{-}COMeC_6H_3)_2$ and $Os(2\text{-}MeC_6H_4)(2\text{-}Me\text{-}4\text{-}COMe\text{-}C_6H_4)_3$. Electrophilic substitution reactions have been tried successfully on π-bonded organometallic compounds, *e.g.* ferrocene [75], although most cyclopentadienyl compounds do not survive the reaction conditions involved in aromatic substitution.

To our knowledge this is the first example of electrophilic substitution in a σ-bonded organometallic aryl compound. Other electrophilic substitution reactions have included mercuration (with $Hg(O_2CMe)_2$, $MeCO_2H$ in thf), nitration (with BF_4NO_2 in CH_2Cl_2) and Friedel-Crafts acylation with Me_3CCOCl, which reacted smoothly and pumped down into a red oil but decomposed on addition of diethyl ether.

(B) *Cis*-Dioxoaryls of osmium(VI)

(iii) Synthesis and structure of $OsO_2(xylyl)_2$

The interaction of osmium tetraoxide with seven equivalents of xylylmagnesium bromide in tetrahydrofuran and subsequent oxidation of the resulting deep red solution leads to the isolation of the diamagnetic air stable Os^{VI} compound, $OsO_2(xylyl)_2$, which can be crystallised as green crystals from hexane or ether.

The compound is thermally and air stable both as a solid and in

solution and is soluble in aromatic, aliphatic and halogenated hydrocarbons, ethers, acetone and acetonitrile but is insoluble in and unaffected by water. Both $OsO_2(mesityl)_2$ and $OsO_2(xylyl)_2$ show greater solubility and stability than their rhenium analogues.

As well as the xylyl peaks, the i.r. spectrum shows two strong peaks at 960 and 915 cm^{-1} both accompanied by shoulders at 970 and 926 cm^{-1} respectively, probably due to lattice strain effects. These are assigned to the $\nu(Os=O)$ stretches of the *cis*-OsO_2 unit, which compare favourably with the mesityl compound.

The ^1H n.m.r. spectrum shows a sharp peak at $\delta 2.37$ readily assigned to the *ortho*-methyls, a triplet at $\delta 6.92$ (1*p*-H) and a doublet at $\delta 7.15$ (2*m*-H). The $^{13}C-\{^1H\}$ spectrum shows the *ortho*-methyls at $\delta 28.9$, and of the four unique aromatic carbons, only three can be seen at $\delta 126.7$, 131.0 and 146.5. This phenomenon occurs in a number of high oxidation state aryl complexes *e.g.* $OsO_2(mesityl)_2$ [19b] and $Os(C_6H_5)_4$ [18b].

The structure of the molecule is shown in Figure 3.4 and selected bond lengths and angles are given in Table 3.3. The surprising result that crystals of $OsO_2(xylyl)_2$ are not isostructural with those of $ReO_2(xylyl)_2$, is also reflected in the molecular structure, which shows some very significant differences. Most noticeable are the O-M-O and C-M-C angles which for OsO_2R_2 show a much greater difference than the corresponding angles in the rhenium complex. This difference may be a reflection on the greater deforming effect of a filled non-bonding orbital in this diamagnetic d^2 Os^{VI} complex when compared with a half-filled orbital, in the d^1 Re^{VI} analogue.

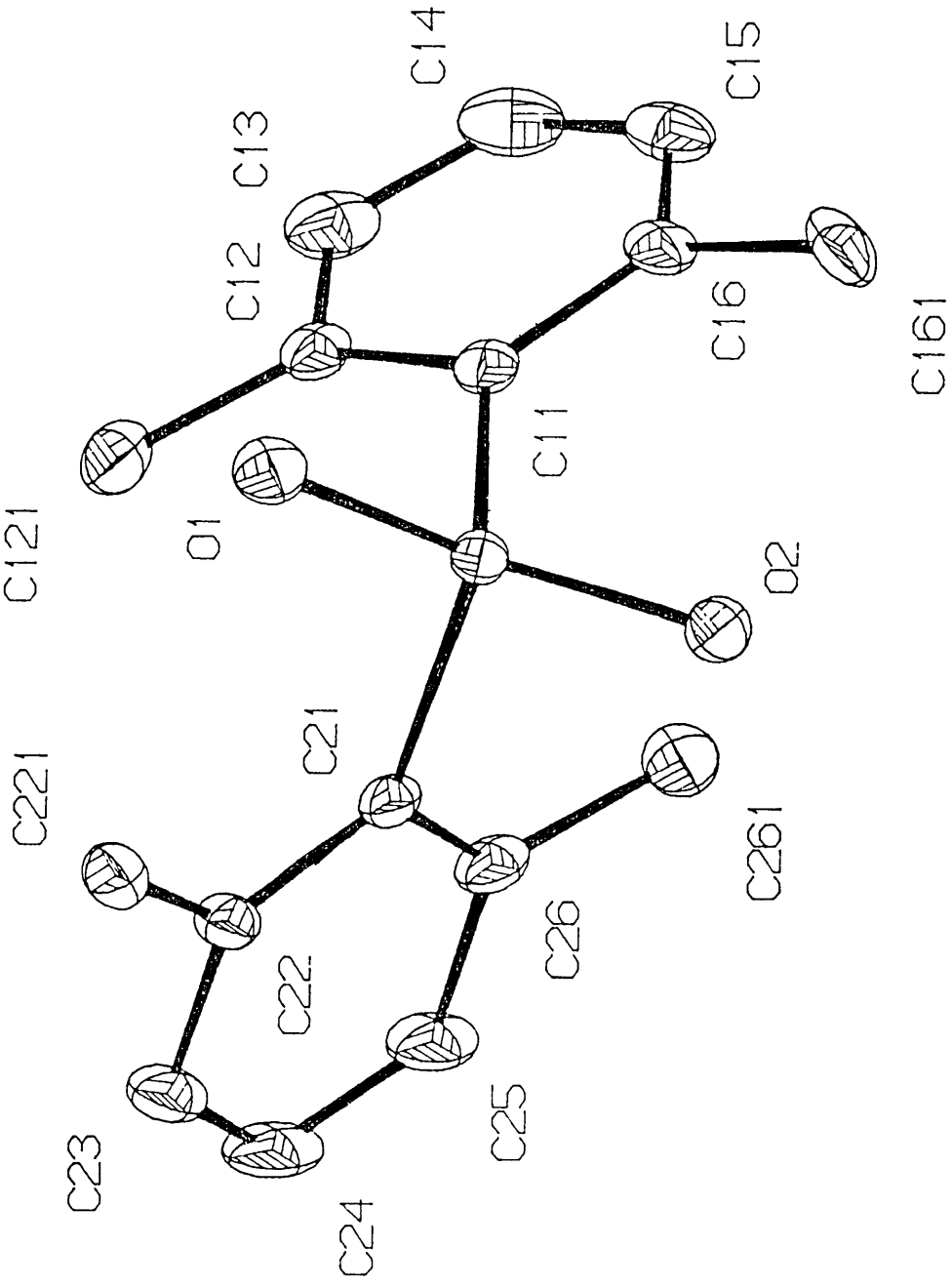


Figure 3.4: The molecular structure of $Os^{VI}O_2(xylyl)_2$.

Table 3.3: Bond lengths (Å) and angles (deg.) for $Os^{VI}O_2(xylyl)_2$.

Bond Lengths

Os-O(1)	1.699
Os-O(2)	1.671
Os-C(11)	2.060
Os-C(21)	2.036
C(11)-C(12)	1.412
C(12)-C(121)	1.492

Bond Angles

O(1)-Os-O(2)	139.2
O(1)-Os-C(11)	101.1
O(2)-Os-C(11)	108.2
O(1)-Os-C(21)	107.5
O(2)-Os-C(21)	98.1
C(11)-Os-C(21)	94.4
Os-C(11)-C(12)	120.86
Os-C(11)-C(16)	118.6
Os-C(21)-C(22)	119.2
Os-C(21)-C(26)	126.15
C(22)-C(21)-C(26)	117.6

The two osmium compounds are almost isostructural; slight differences arise with the O-Os-O angle of the xylyl compound which is larger than that of the mesityl (139.2° and 131.1° respectively), making the C-Os-C angle of the xylyl (94.4°) smaller than that of the mesityl (96.0°).

From the original deep red reaction solutions prior to oxidation some red crystals can be crystallised from diethyl ether but no reasonable data could be obtained of the product, presumably the paramagnetic $[(xylyl)_2O_2Os]_2Mg(thf)_2$ solvated species.

Once again, as in the case of rhenium, the use of a di-*ortho*-substituted aryl (xylyl, mesityl) as opposed to a mono-*ortho*-substituted aryl (*o*-tolyl) has a significant effect on the formation of the isolable products (OsO_2R_2 and OsR_4 respectively).

Addition of small Grignards to the $OsO_2(xylyl)_2$ compound *e.g.* MeMgI, Me_3SiCH_2MgCl and Me_3CCH_2MgCl) turns green solutions bright red instantly, even at -78°C. The compounds however, seem to be highly unstable and decompose rapidly even at low temperatures. Addition of stabilising compounds like PMe_3 was not investigated. $OsO_2(xylyl)_2$ does not react with isocyanates RNCO (R = *c*-C_6H_{11}, ^{t}Bu and Me_3Si) even at refluxing toluene temperatures. Reduction of the compound with thionyl chloride again produces a red solution, but the oily mixtures could not be identified.

Experimental

Osmium tetraoxide was from Johnson Matthey PLC. $AlCl_3$ was sublimed prior to use and all other experimental procedures are given in the experimental of Chapter 1.

3.1) Tetrakis(4-^{t}butylphenyl)osmium(IV)

To a stirred solution of OsO_4 (0.5 g, 1.98 mmol) in thf (40 cm^3) was added 4-*tert*-butylphenylmagnesium bromide (19.7 cm^3 of a 0.7 mol dm^{-3} solution in Et_2O, 14 mmol) and the mixture warmed to room temperature. The volatile materials were removed under reduced pressure and were extracted into a hexane/ether mixture (20 cm^3: 20 cm^3 × 3), filtered and reduced to dryness. The resulting oil was dissolved in diethyl ether (30 cm^3), concentrated to *ca.* 15 cm^3 and cooled to -20°C overnight to yield dark red crystals.

Yield: 0.4 g, 28%.

I.r.: 1615w, 1500s, 1395s, 1382(sh), 1270s, 1255(sh), 1208m, 1120s, 1060(br), 1035m, 1006m, 940(sh), 930w, 851(sh), 825vs, 760m, 735s, 710w, 590w, 560s.

Mass Spectrum: m/e 517 (10%) $OsR(R\text{-}Bu)(R\text{-}Me)^+$, 456 (1%) OsR_2^+, 266 (56%) R_2^+, 251 (100%) $R_2\text{-}Me^+$, 133 (4%) R^+, 118 (11%) $R\text{-}Me^+$, 57 (23%) Bu^+.

N.m.r. ^1H: δ1.41 (9H, *s*, CMe_3), 7.54 (4H, *m*, C_6H_4); $^{13}C\text{-}\{^1H\}$: 31.4 (s, CMe_3), 34.5 (s, CMe_3), 125.6, 126.7, 138.3 and 150.0 (s, C_6H_4).

3.2) Tris(2-methylphenyl)(2-methyl-4-acetylphenyl)osmium(IV)

Tetrakis(2-methylphenyl)osmium(IV) (0.205 g, 0.37 mmol) and $AlCl_3$ (0.44g, 3.26 mmol) were suspended in CH_2Cl_2 (30 cm^3) at -78°C. Acetic anhydride (0.15 g, 1.46 mmol) was added and the mixture warmed slowly to room temperature and held for 2h. The solution was filtered and reduced to dryness *in vacuo*, and the residue extracted in diethyl ether (3 × 10 cm^3) and concentrated to *ca.* 5 cm^3. The mixture was eluted through a Kieselgel 60H column with ether and the second band was collected and recrystallised from hexane

($10\ cm^3$).

Yield: 0.03 g, 14%

I.r.: 1677s, 1575s, 1295s, 1253s, 1192m, 1160m, 1121(sh), 1099s, 1095(sh), 999s, 986(sh), 970m, 901w, 884w, 825m, 746s.

Mass Spectrum: m/e 224 (34%) RR'^+, 209 (68%) $RR'\text{-}Me^+$, 182 (31%) R_2^+, 167 (31%) $R_2\text{-}Me^+$, 152 (8%) $R_2\text{-}2Me^+$, 133 (16%) R'^+, 118 (27%) $R'\text{-}Me^+$, 91 (100 %) $C_7H_7^+$. R = *o*-methylphenyl and R' = 2-methyl-4-acetylphenyl.

3.3) *cis*-Dioxodixylylosmium(VI)

To a stirred solution of OsO_4 (0.5 g, 1.98 mmol) in thf ($35\ cm^3$) at -78°C was added 2,6-dimethylphenylmagnesium bromide ($40.5\ cm^3$ of a 0.3 mol dm^{-3} solution in Et_2O, 13.8 mmol). The mixture was allowed to warm slowly to room temperature and held for 1h. The solvent was removed *in vacuo* and oxygen saturated hexane ($60\ cm^3$) was added to the residue and the mixture stirred overnight. The green filtered extract was concentrated to *ca.* $15\ cm^3$ and cooled to -20°C to give green crystals.

Yield: 0.38 g, 44%.

I.r.: 1556m, 1261w, 1238s, 1196w, 1165(sh), 1160s, 1117w, 1025(sh), 1010s, 1000m, 960s, 926(sh), 915(vsbr), 890(sh), 770vs, 750m, 706s, 556m.

Mass Spectrum: m/e 434 (58%) $^{192}OsO_2R_2^+$, 432 (42%) $^{190}OsO_2R_2^+$, 431 (28%) $^{189}OsO_2R_2^+$, 432 (23%) $^{188}OsO_2R_2^+$, 416 (7%) $^{190}OsOR_2^+$, 400 (7%) $^{190}OsR_2^+$, 327 (18%) $^{190}OsO_2R^+$, 313 (49%) $^{192}OsOR^+$, 311 (35%) $^{190}OsOR^+$, 298 (21%) $^{192}OsO(R\text{-}Me)^+$, 296 (17%) $^{190}OsO(R\text{-}Me)^+$, 295 (11%) $^{190}OsR^+$, 210 (42%) R_2^+, 195 (12%) $R_2\text{-}Me^+$, 180 (14%) $R_2\text{-}2Me^+$, 105 (95%) R^+, 91 (100%) $C_7H_7^+$, 77 (68%) $C_6H_5^+$. R = 2,6-dimethylphenyl.

N.m.r. ^{1}H: δ2.37 (6H, s, *o-Me*), 6.92 (1H, t, 1*p-H*) and 7.15 (2H, d, 2*m-H*);

$^{13}C-\{^{1}H\}$: 28.9 (s,*o*-Me) and 126.7, 131.0 and 146.5 (s, ring carbons).

CHAPTER 4

CHLOROTRIS(TRIMETHYLSILYLMETHYL) TRIMETHYLSILYLMETHYLIDYNE RHENIUM(VII)

Chlorotris(trimethylsilylmethyl)trimethylsilylmethylidyne Rhenium(VII)

Introduction

The first monomeric alkylidyne complexes, *trans* - $X(CO)_4M{\equiv}CR$ (M = Mo and W), were prepared by treating an alkylidene complex with BX_3 [76] in 1973. Higher oxidation state species of the type $M(CCMe_3)(CH_2CMe_3)_3$ have been prepared by treating $MoCl_5$ or WCl_6 with five or six equivalents of neopentyllithium [77].

Interest in d^o alkylidyne complexes increased after it was discovered that d^o alkylidene complexes of tungsten will metathesize olefins [78], and there was some reason to expect that d^o alkylidyne complexes would metathesize acetylenes [79].

Schrock and co-workers have prepared numerous rhenium alkylidyne complexes [80], mostly by reactions of $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$ with lithium butoxide and lithium neopentyl to yield $Re(CCMe_3)(CHCMe_3)(OCMe_3)_2$ and $Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$ respectively. Protonation of the latter compound with HCl yields the analogous neopentylidyne compound $Re(CCMe_3)(CH_2CMe_3)_3Cl$.

We report in this chapter the synthesis of the first monomeric rhenium(VII) trimethylsilylmethylidyne complex.

Results and Discussion:

The alkylation of $ReCl_4(thf)_2$ in tetrahydrofuran with trimethylsilylmethylmagnesium chloride under nitrogen leads to the dinitrogen complex [38], $[Re(CH_2SiMe_3)_4]_2N_2$, as well as low yields of bis(μ-trimethylsilylmethylidyne)tetrakis(trimethylsilylmethyl)dirhenium [81]. A third minor product from this reaction, a hexane soluble yellow air-sensitive crystalline solid $ReCl(CSiMe_3)(CH_2SiMe_3)_3$ [82] has now been isolated. (see Figure 4.1).

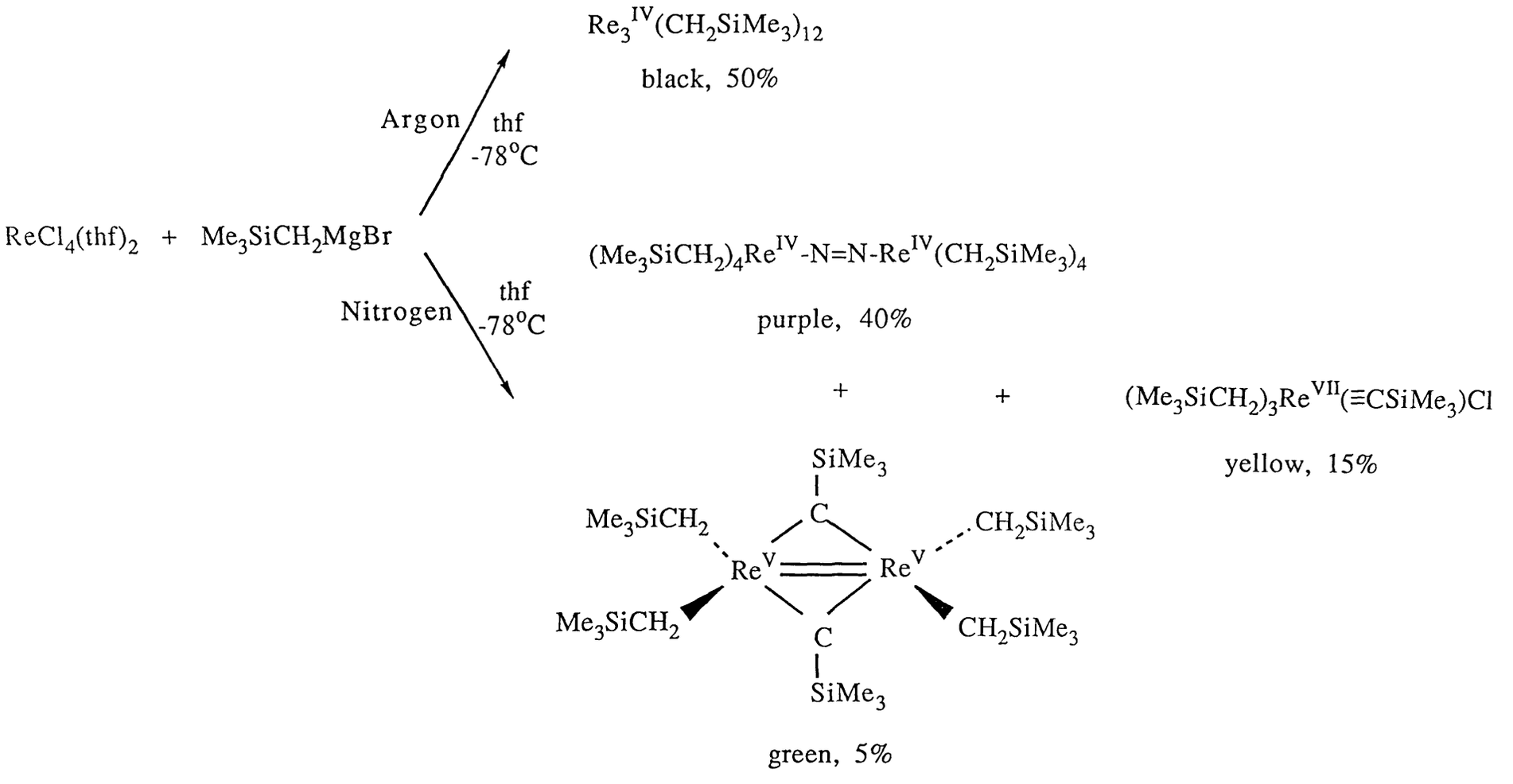


Figure 4.1: Interaction of $ReCl_4(thf)_2$ with Me_3SiCH_2MgCl

Reacting the same starting reagents under argon, however, yields only one product, dodeca(trimethylsilylmethyl)triangulotrirhenium [38], $Re_3(CH_2SiMe_3)_{12}$. The alkylidyne can be crystallised from hexane as monoclinic crystals. The spectroscopic data are in agreement with the structure as determined. There are singlets in the ^1H n.m.r. spectrum at δ 0.22 and 0.15 (relative intensity 27:9) indicating the trimethylsilylmethyl and trimethylsilylmethylidyne methyl protons respectively; a singlet at δ 3.22 (relative intensity 6) can be assigned to the methylene hydrogens, whose low field value is characteristic of rhenium trimethylsilylmethyl compounds [19a].

The mass spectrum shows the molecular ion m/e 568 (13%) with the correct rhenium isotope pattern, although the base mass is m/e 553 (M^+-Me). Sequential loss of CH_2SiMe_3 groups are not well defined, due to the facile loss of CH_3 groups.

The molecular structure as determined by X-ray crystallography is shown in Figure 4.2, and confirms the structure predicted by Schrock *et al.* [80] for the analogous neopentyl neopentylidyne complex $ReCl(CCMe_3)(CH_2CMe_3)_3$. Selected bond lengths and angles are given in Table 4.1. The metal has a trigonal bipyramidal configuration, with the trimethylsilylmethylidyne and chlorine ligands axial. The Re-C bonds to the equatorial trimethylsilylmethyl ligands are bent away slightly from the multiply bonded alkylidyne, as is usually found, and the Re-C-Si angles in the alkyls are somewhat greater than tetrahedral due to steric repulsions involving the $SiMe_3$ groups. Otherwise, geometry parameters are as expected.

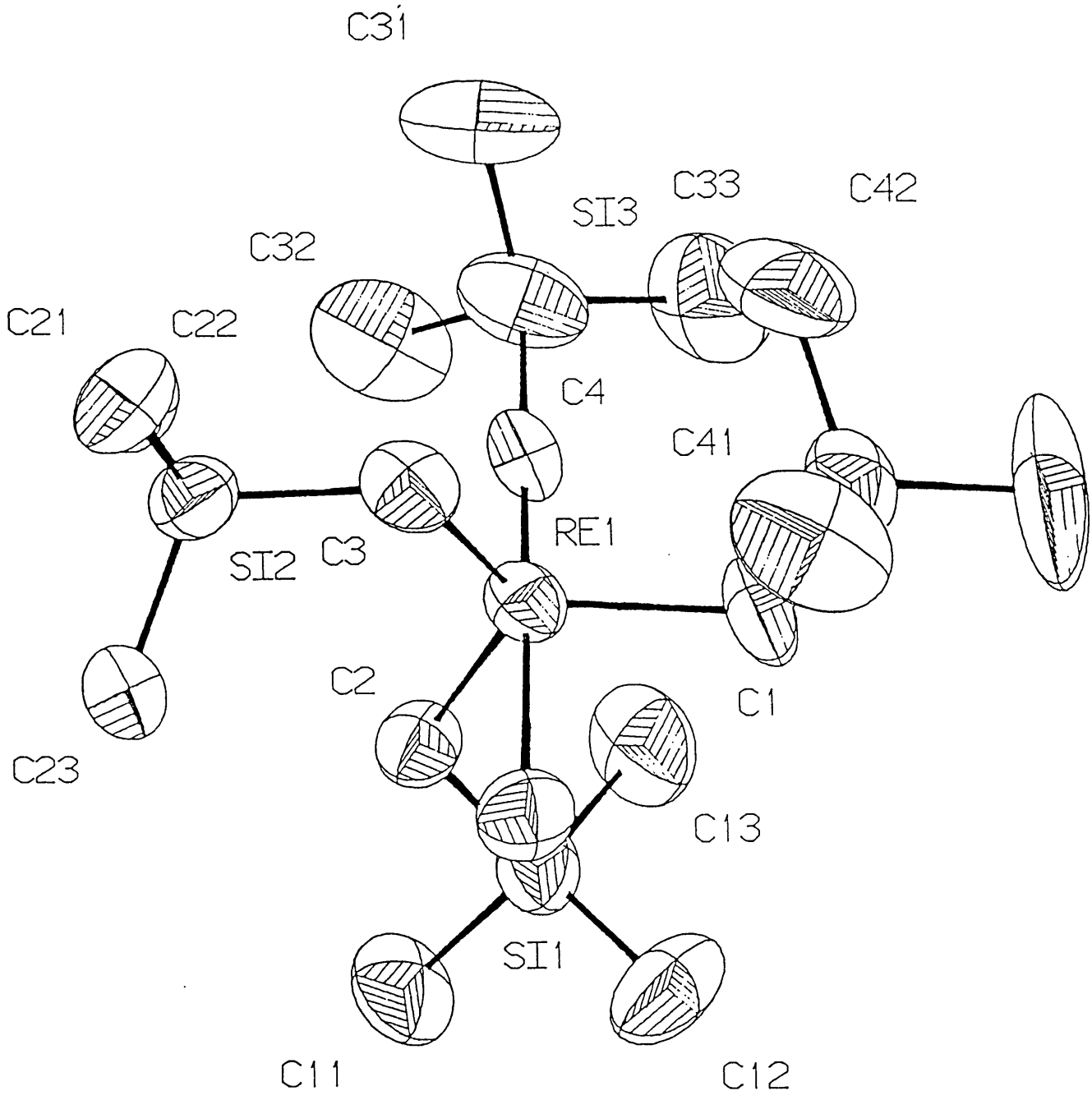


Figure 4.2: The molecular structure of $Re(CSiMe_3)(CH_2SiMe_3)_3Cl$.

Table 4.1: Selected bond lengths and angles for $Re(CSiMe_3)(CH_2SiMe_3)_3Cl$.

(a) Bond Lengths (Å)

Cl(1)-Re(1)	2.523(6)	C(1)-Re(1)	2.084(13)
C(2)-Re(1)	2.059(12)	C(3)-Re(1)	2.052(12)
C(4)-Re(1)	1.726(11)	C(1)-Si(1)	1.850(13)
C(11)-Si(1)	1.831(18)	C(12)-Si(1)	1.826(20)
C(13)-Si(1)	1.751(19)	C(2)-Si(2)	1.868(12)
C(21)-Si(2)	1.845(15)	C(22)-Si(2)	1.859(16)
C(23)-Si(2)	1.860(16)	C(3)-Si(3)	1.927(14)
C(31)-Si(3)	1.842(14)	C(32)-Si(3)	1.852(14)
C(33)-Si(3)	1.845(15)	C(4)-Si(4)	1.893(12)
C(41)-Si(4)	1.819(16)	C(42)-Si(4)	1.843(18)
C(43)-Si(4)	1.805(18)		

(b) Bond Angles (deg.)

C(1)-Re(1)-Cl(1)	87.9(4)	C(2)-Re(1)-Cl(1)	86.1(4)
C(2)-Re(1)-C(1)	118.2(5)	C(3)-Re(1)-Cl(1)	85.4(4)
C(3)-Re(1)-C(1)	119.5(5)	C(3)-Re(1)-C(2)	121.2(5)
C(4)-Re(1)-Cl(1)	179.5(3)	C(4)-Re(1)-C(1)	92.0(6)
C(4)-Re(1)-C(2)	94.4(5)	C(4)-Re(1)-C(3)	94.3(5)
C(11)-Si(1)-C(1)	111.2(7)	C(12)-Si(1)-C(1)	113.0(8)
C(12)-Si(1)-C(11)	105.2(10)	C(13)-Si(1)-C(1)	106.0(8)
C(13)-Si(1)-C(11)	110.6(12)	C(13)-Si(1)-C(12)	110.9(11)
C(21)-Si(2)-C(2)	105.8(6)	C(22)-Si(2)-C(2)	113.0(6)
C(22)-Si(2)-C(21)	107.6(8)	C(23)-Si(2)-C(2)	110.5(6)
C(23)-Si(2)-C(21)	109.3(7)	C(23)-Si(2)-C(22)	110.5(8)
C(31)-Si(3)-C(3)	105.8(7)	C(32)-Si(3)-C(3)	110.4(6)
C(32)-Si(3)-C(31)	110.6(6)	C(33)-Si(3)-C(3)	112.8(6)
C(33)-Si(3)-C(31)	107.6(7)	C(33)-Si(3)-C(32)	109.6(7)
C(41)-Si(4)-C(4)	109.7(7)	C(42)-Si(4)-C(4)	108.8(7)
C(42)-Si(4)-C(41)	111.2(10)	C(43)-Si(4)-C(4)	105.1(8)
C(43)-Si(4)-C(41)	111.3(9)	C(43)-Si(4)-C(42)	110.5(8)
Si(1)-C(1)-Re(1)	118.7(7)	Si(2)-C(2)-Re(1)	119.5(7)
Si(3)-C(3)-Re(1)	116.2(6)	Si(4)-C(4)-Re(1)	178.8(6)

Experimental:

All details on the spectrometers used and of the experimental procedures are given in the experimental section of Chapter 1.

4.1) Chlorotris(trimethylsilylmethyl)trimethylsilylmethylidyne rhenium(VII)

To a stirred suspension of $ReCl_4(thf)_2$ (0.51g, 1.08 mmol) in thf ($50cm^3$) at -78° C was added trimethylsilylmethylmagnesium chloride ($6.0cm^3$ of a 0.73 mol dm^{-3} solution in diethylether, 4.3 mmol) under nitrogen. The solution was warmed slowly and held at room temperature for 1h. The resulting purple solution was evaporated and the residue extracted into hexane (3 x 30 cm^3), concentrated to about 50 cm^3 and cooled to -20°C overnight.

Yield: 0.06g, 10%; m.p. 120-122°C.

Found: C, 33.3; H, 7.4; Cl, 6.1. Calc. for $ReC_{16}H_{42}Si_4Cl$: C, 33.8; H, 7.4: Cl, 6.2%.

I. r. (cm^{-1}): 1410m, 1336S, 1248 vs, 1179s, 1060w, 1020w, 971 (sh), 935 (sh), 906s, 845 vs, 780 (sh), 755m, 701 (sh), 679 m and 622 m.

N.m.r. ^1H: 3.22 (6H, S, CH_2SiMe_3), 0.22 (27H, S, CH_2SiMe_3) and 0.15 (9H, S, $Re{\equiv}C\text{-}SiMe_3$).

Mass Spectrum: m/e, 568 (13%), $[Re(\equiv CSiMe_3)(CH_2SiMe_3)_3Cl]^+$; 553 (100%), $[Re(\equiv CSiMe_3)(CH_2SiMe_3)_3\ Cl - Me]^+$; 73 (87%), $SiMe_3^+$.

CHAPTER 5

HOMOLEPTIC CYCLOALKYL COMPOUNDS OF CHROMIUM

Homoleptic Cycloalkyl Compounds of Chromium

Introduction

Transition metal complexes containing alkyl or aryl ligands have proliferated in the past two decades. For the early transition metals, Ti, Zr, Hf, V, Cr [13], for Mo [83], W [84] and also for Mn [42,43], Fe [43] and Co [43,85] alkyls and/or aryls have been isolated and several have been crystallographically characterised: $M(CH_2C_6H_5)_4$ (M = Ti [86], Zr [87], or Hf [86]), $V(2,4,6\text{-}Me_3C_6H_2)_4$ [88], $Cr(CH_2CMe_2Ph)_4$ [89], and $Cr(CPh{=}CMe_2)_4$ [90].

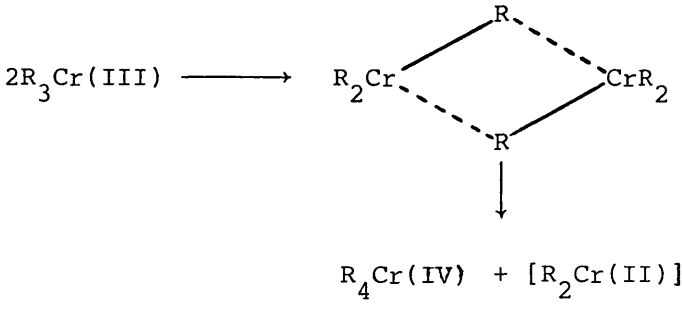
Some elimination stabilized cyclohexyl and cyclopentyl compounds have recently been synthesised: $R_2MoO_2(bpy)$ [91], (R=c-C_5H_9 and c-C_6H_{11}, bpy = 2,2'-bipyridyl) and Bergman's hydridocyclohexyliridium(III) compound [92], (η^5-C_5Me_5)(PMe_3)IrH(c-C_6H_{11}), made from the photolysis of cyclohexane with the dihydride, (η^5-C_5Me_5)(PMe_3)IrH_2.

Since the synthesis of tetrakis(trimethylsilylmethyl)chromium(IV) by Wilkinson and co-workers in 1971 [10b], several tetraalkyl chromium(IV) compounds have been prepared. Many have employed alkyl ligands of the type $-CH_2R$, where R is such that there is no β-hydrogen (*e.g.* R = $-C(Me)_3$ [93], $-Si(Me)_3$ [10b], $-C(Ph)_3$ [93], and $-CMe_2Ph$ [93]. This excludes the possibility of β-hydrogen elimination [13,94] where facile decomposition *via* intramolecular transfer of hydrogen from a β-carbon to the metal can occur. Further stable examples include $Cr(1\text{-norbornyl})_4$ and $Cr(1\text{-camphyl})_4$ [43], and although both ligands contain β-hydrogens, β-elimination is unfavourable because unsaturation at a bridgehead carbon would result (Bredt's Rule) [95].

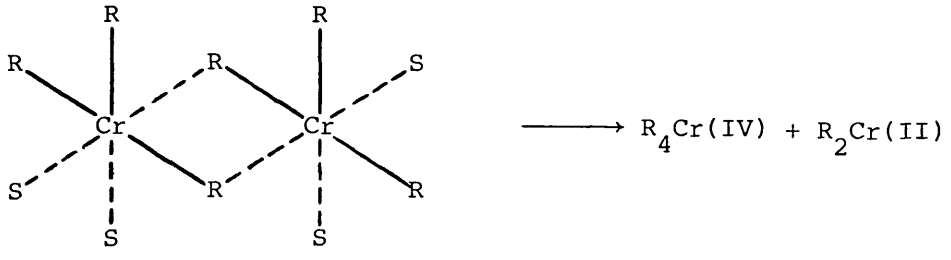
Kruse [96] and Wilkinson and co-workers [10b,93] simultaneously isolated several tetraalkylchromium(IV) compounds namely $Cr(CMe_3)_4$ [96],

$Cr(CH_2CMe_3)_4$ [93,96], $Cr(CH_2CMe_2Ph)_4$ and $Cr(CH_2CPh_3)_4$ [93]. The compound $Cr(CMe_3)_4$ (with 36 β-hydrogens) is stable because the steric bulk of the *tert*-butyl groups prevents the required geometry for the β-elimination transition state. The tetraalkylchromium(IV) compounds have been prepared by the interaction of $CrCl_3(thf)_3$ or $Cr(OCMe_3)_4$ with organolithium or organomagnesium reagents. The interaction of $CrCl_3(thf)_3$ with organomagnesium halides (in stoichiometric ratios of 1:4) in diethyl ether yields the tetra(organo)chromium(IV) compounds, either *via* a disproportionation or an oxidation reaction [97].

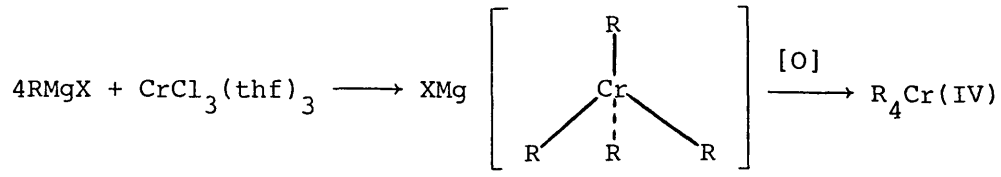
The disproportionation reaction may proceed *via* an electron transfer from one chromium atom to another in a dimeric bridged intermediate:



or *via* an octahedral dimeric intermediate disproportionation:



The "oxidation reaction" may proceed *via* an intermediate tetrahedral tetraalkylchromate(III) complex, which by loss of an electron would give the tetraalkylchromium(IV) compound directly:



In this work, cycloalkylmagnesium halides were used to alkylate $CrCl_3(thf)_3$ giving tetracycloalkylchromium(IV) compounds.

Results and Discussion

1. Synthesis and Structure of tetrakis(cyclohexyl)chromium(IV).

The interaction of $CrCl_3(thf)_3$ with four equivalents of cyclohexyl Grignard yields dark red crystals of the paramagnetic compound $Cr(C\text{-}C_6H_{11})_4$. The compound (Cr^{IV}, d^2) has a magnetic susceptibility of 2.77 B.M. determined in the solid state at ambient temperature, in accordance with other Cr(IV) tetraalkyls [10b,93].

The compound shows astonishing thermal stability, decomposing only *ca.* 200°C and does not react with CO or H_2 even under 10 atm. at 70°C, but will react rapidly with NO, although the nature of the product could not be determined. In solution and in the solid state the compound will decompose when exposed to oxygen over relatively short periods of time.

The infrared spectrum of $Cr(C\text{-}C_6H_{11})_4$ shows bands characteristic of the cyclohexyl ligand. For a near-tetrahedral structure two i.r. active bands are expected for Cr-C between 400-500cm^{-1} [93], and bands at 487 and 410cm^{-1} are observed.

The mass spectrum shows the parent ion, m/e 384 (4%), $Cr(C_6H_{11})_3^+$ m/e 301 (2%), $Cr(C_6H_{11})_2^+$ m/e 218 (14%), and the base peak m/e 135 (100%)

corresponding to $Cr(C_6H_{11})^+$. The cyclohexyl ligand, m/e 83 (26%) is also present.

The molecular structure of the chromium cyclohexyl compound [18b] is shown in Figure 5.1; selected bond lengths and angles are collected in Table 5.1. The compound is sited on a crystallographic two-fold axis and the effective molecular symmetry approaches $\bar{4}$. Thus the two independent Cr-C bond lengths are equal within the limits of error, the twists of the two independent rings [*i.e.* representative torsion angles about the Cr-C bonds, *e.g.* C(n1')-Cr-C(n1)-C(n2) (n = 1 or 2)], differ by only 1 or 2°, and the dihedral angle between the C(11')-Cr-C(11), and the C(21')-Cr-C(21) planes is 91.1°.

The CrC_4 tetrahedra are slightly flattened in the direction of the two-fold axis with C(11,11')-Cr-C(21,21') 114.5° and C(11,11')-Cr-C(21,21') 106.2 - 107.8°. Unfortunately, the X-ray crystal structure of $Cr(CH_2CMe_2Ph)_4$ [89] is of insufficient accuracy (R = 0.127) to draw any comparison with that of the tetracyclohexylchromium. The X-ray structure of $Cr(CPh = CMe_2)_4$ [90] shows the mean Cr-C bond length as 2.036Å and the CrC_4 tetrahedral bond angles in the range 105.3 - 116.4°. Inter- and intra-ligand interactions clearly dominate the geometry of the tetraalkenylchromium compound.

The scarcity of transition metal cyclohexyls [98] has been assumed to be due to facile β-hydride transfers and the only previously reported homoleptic transition metal compound (apart from $Os(C\text{-}C_6H_{11})_4$ [18b] and $Ru(C\text{-}C_6H_{11})_4$- see Chapter 1) $Ti(C\text{-}C_6H_{11})_4$ [22] decomposes above -30°C.

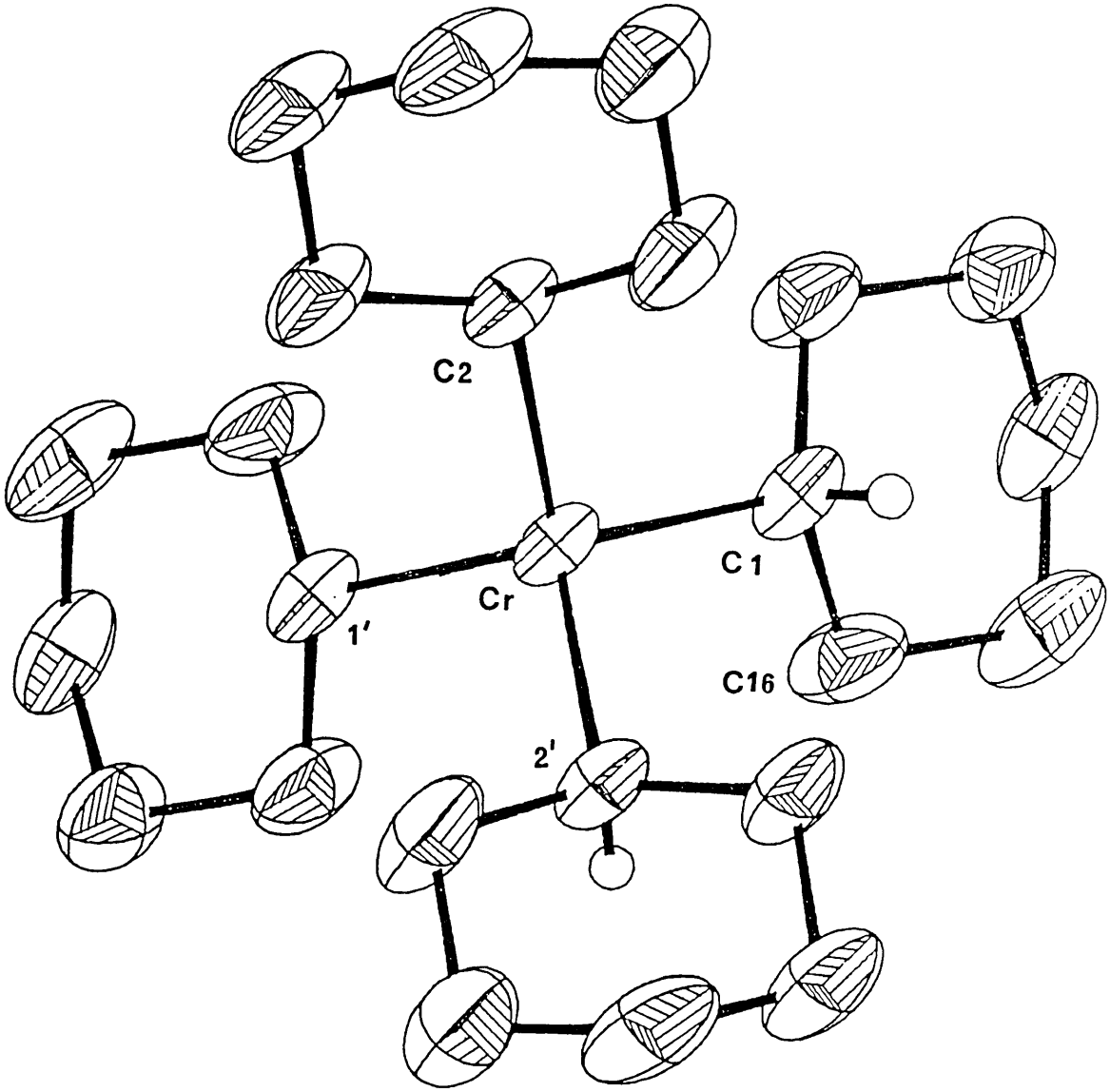


Figure 5.1: The molecular structure of $Cr(C\text{-}C_6H_{11})_4$

Table 5.1: Bond lengths and angles for $Cr(C\text{-}C_6H_{11})_4$.

Bond Lengths (Å) for $Cr(C\text{-}C_6H_{11})_4$

Cr - C(11)	2.009(4)
Cr - C(21)	2.010(4)

Bond Angles (deg.) for $Cr(C\text{-}C_6H_{11})_4$

C(11) - Cr - C(11')	114.5(2)
C(21) - Cr - C(21')	114.5(2)
C(11) - Cr - C(21)	107.8(2)
C(11') - Cr - C(21)	106.2(2)
Cr - C(11) - C(12)	116.0(2)
Cr - C(11) - C(16)	112.6(3)
Cr - C(21) - C(22)	116.1(3)
Cr - C(21) - C(26)	112.8(3)
C(12) - C(11) - C(16)	111.2(3)
C(22) - C(21) - C(26)	110.9(3)

2. Synthesis of Cyclopentyl, Cycloheptyl and Cyclooctyl Chromium(IV) Compounds

The interaction of $CrCl_3(thf)_3$ with bis(cyclopentyl)magnesium, cycloheptylmagnesium bromide and cyclooctylmagnesium bromide in diethyl ether or tetrahydrofuran at -78°C yielded deep red solutions of the tetrakis(cycloalkyl)chromium(IV) species. The compounds were stable in solution at room temperature for short periods of time, however the compounds underwent decomposition in the solid state.

Attempts were made to stabilize the compounds with donor ligands (*e.g.* PMe_3 and pyridine) but all attempts resulted in decomposition.

All the compounds in this chapter have been characterised by electron spin resonance (E.S.R).

The Electron Spin Resonance Spectra of tetrakis(cycloalkyl) chromium(IV) Complexes

A red hexane solution of $Cr(C\text{-}C_6H_{11})_4$, prepared under anaerobic conditions, gives a broad mid-field line which, in frozen hexane at 77K (*X*-band), splits into two (g = 2.08, 1.82), while at the same time a new, weak, narrow line appears at g = 1.95. As previously stated [93,99] this new peak cannot be assigned to any transition of the $^3A_2$ ground state of the alkyl. It is clear that the $g \simeq 2$ resonance is due to some magnetically concentrated phase that separates from the solution at low temperatures, presumably because of reduced solubility. A hexane solution of $Cr(C\text{-}C_6H_{11})_4$, that is not more than 10^{-3} molar, does not show the sharp line. A low field line is also observed at g = 3.71, probably due to a forbidden transition ($\Delta m = 2$). (see Figure 5.2).

The experimental data for the other tetrakis(cycloalkyl)chromium(IV) compounds are collected in Table 5.2. In most cases, the thf solvent

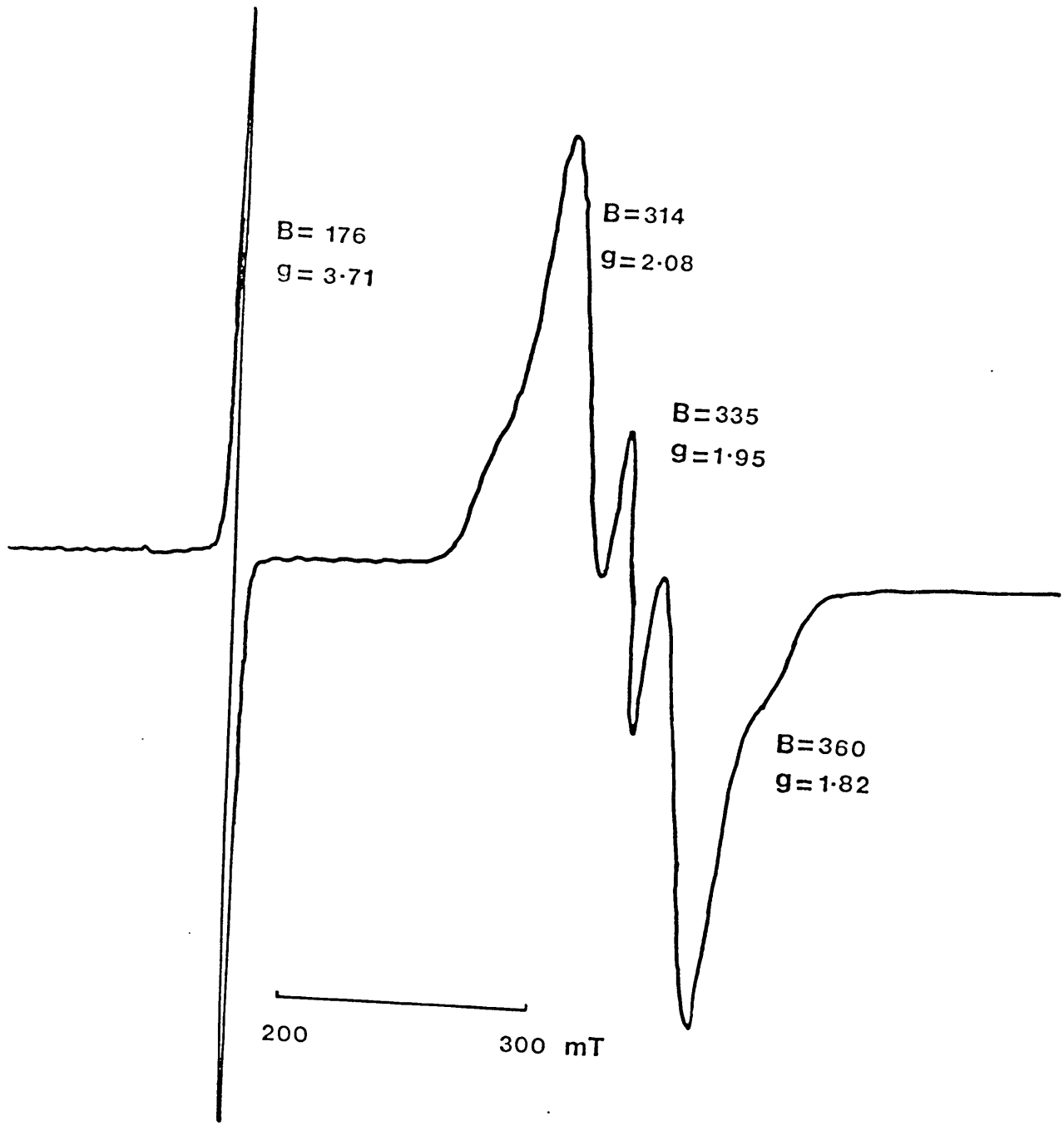


Figure 5.2: The E.S.R. spectra of $Cr(C\text{-}C_6H_{11})_4$

Table 5.2: Electron Spin Resonance Parameters for Chromium Cycloalkyl Complexes.

	Mid-field transitions $\Delta m = 1$			Low field transition $\Delta m = 2$
			new spike	
	g	*g*	*g*	*g*
$Cr(C_5H_9)_4$	2.10	1.85	1.97	3.77
$Cr(C_6H_{11})_4$	2.08	1.82	1.95	3.71
$Cr(C_7H_{13})_4$ [(a)]	2.41	1.76	2.04	4.10
$Cr(C_8H_{15})_4$	2.03	1.98	2.00	4.03

data collected in hexane except (a) thf.

was removed at low temperatures under reduced pressures, and the residue extracted in cold hexane for the E.S.R. analysis.

Experimental:

E.S.R.: Varian E12 (*X*-band) instrument in hexane or tetrahydrofuran glasses at 77K. $CrCl_3(thf)_3$ [100] was prepared as previously reported. Other details on the spectrometers used and of the experimental procedures are given in the experimental section of Chapter 1.

5.1) Synthesis of Tetrakis(cyclohexyl)chromium(IV)

Cyclohexylmagnesium bromide ($26.7cm^3$ of a 1.0 mol dm^{-3} solution in Et_2O, 26.7mmol) was added to a stirred suspension of $CrCl_3(thf)_3$ (2.5g, 6.7mmol) in Et_2O ($40cm^3$) at -78°C and the mixture warmed to room temperature. The volatile materials were removed under reduced pressure and the residue was extracted with hexane ($2x30cm^3$). Concentration of the filtered extracts to *ca.* $35cm^3$ and cooling overnight (-5°C) afforded dark red crystals. Yield: 0.56g, 22%. m.p. *ca.* 200° dec. (Found: C, 74.2; H, 11.3. $C_{24}H_{44}Cr$ requires C, 74.9; H, 11.5). I.r.: 2908s, 2835(sh), 2772m, 1425s, 1397s, 1340w, 1320w, 1278w, 1245(sh), 1150s, 1135s, 1022m, 1000m, 795s, 602s, 487m and 410m cm^{-1}. Mass Spectrum: $Cr(C_6H_{11})_4^+$, 384 (4%), $Cr(C_6H_{11})_3^+$, 301 (2%), $Cr(C_6H_{11})^+$, 135 (100%) and $C_6H_{11}^+$, 83 (26%).

5.2) Synthesis of Tetrakis(cyclopentyl)chromium(IV)

Dicyclopentylmagnesium ($7.3cm^3$ of a 0.83 mol dm^{-3} solution in Et_2O, 6.1mmol) was added to a stirred suspension of $CrCl_3(thf)_3$ (0.57g, 1.52mmol) in Et_2O ($40cm^3$) at -78°C. The solution was warmed slowly and the volatile materials were removed under reduced pressure at

-30°C. The residues were extracted into hexane (2x30cm^3), filtered and characterised by E.S.R. spectroscopy.

5.3) Synthesis of Tetrakis(cycloheptyl)chromium(IV)

As above except the $CrCl_3(thf)_3$ (1.10g, 2.94mmol) was alkylated with cycloheptylmagnesium bromide (10.8cm^3 of a 1.10 mol dm^{-3} solution in Et_2O, 12mmol) in thf (30cm^3) at -78°C. The volatile materials were removed at -30°C and the residues were dissolved in thf (15cm^3), filtered and characterised by E.S.R. spectroscopy.

5.4) Synthesis of Tetrakis(cyclooctyl)chromium(IV)

As above except the $CrCl_3(thf)$ (0.6g, 1.6mmol) was alkylated with cyclooctylmagnesium bromide (11.7cm^3 of a 0.55 mol dm^{-3} solution in Et_2O, 6.4mmol) in Et_2O (40cm^3) at -78°C. The volatile materials were removed at -30°C and the residues were extracted in hexane (3x20cm^3), filtered and characterised by E.S.R. spectroscopy.

PUBLICATIONS

1. Nitrosation of Alkenes by Nitric Oxide: Crystal Structures of bis(1-nitroso-2-nitro-cyclohexane) and bis(1-nitroso-2-nitro-1-phenylethane). K.W. Chiu, P.D. Savage, G. Wilkinson, and D.J. Williams. *Polyhedron*, 1985, **4**, 1941.

2. The Synthesis and X-ray Crystal Structures of Homoleptic Tetrahedral Aryls of Osmium(IV) and of Cyclohexyls of Ruthenium, Osmium and Chromium(IV). P. Stavropoulos, P.D. Savage, R.P. Tooze, G. Wilkinson, B. Hussain, M. Motevalli, and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1987, 557.

3. Synthesis and Molecular Structure of Chlorotris(trimethylsilylmethyl)trimethylsilylmethylidyne Rhenium(VII). P.D. Savage, G. Wilkinson, M. Motevalli, and M.B. Hursthouse, *Polyhedron*, 1987, **6**, 1599.

4. The Synthesis and X-ray Crystal Structures of Homoleptic Tetrahedral Aryls of Rhenium(IV) and Ruthenium(IV) and the X-ray Crystal Structures of Oxotetrakis(*o*-methylphenyl) rhenium(VI). P.D. Savage, G. Wilkinson, M. Motevalli, and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, accepted for publication.

5. The Synthesis and X-ray Crystal Structures of High Oxidation State Imido-Aryls and Oxo-Aryls of Rhenium. C.J. Longley, P.D. Savage, B. Hussain, M.B. Hursthouse, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, submitted for publication.

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