COMPLEX CHEMISTRY OF TRANSITIONAL METALS WITH TRIMETHYLSILYLMETHYL AND CARBOXYLATO FUNCTIONS

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ABSTRACT.

Factors governing the stability of transition metal alkyl complexes are discussed, with particular reference to alkyl ligands in which a β-elimination process is inhibited. The trimethylsilylmethyl ligand is found to be a good example of this, and stable complexes of this ligand with several transition metals have been prepared, using a variety of supporting π-bonding ligands. Neopentyl analogues have also been prepared for a comparison of the stabilities. Complexes with bridging alkyl groups, in which β-elimination is sterically prevented, are also discussed. The i.r. and n.m.r. spectra of the compounds are interpreted.

Carboxylato complexes of ruthenium are described, especially those of the trinuclear oxygen-centred type. Reactions of these trinuclear oxo-acetato complexes with several ligands are investigated. The trinuclear structure is not always retained, giving mono- and binuclear derivatives. The compounds are discussed in terms of their magnetic and electrochemical properties.

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Lastly, my thanks to Frank for his companionship and continual encouragement during the past three years.

But I ask no questions,
  no one asks any questions,
Because it's all quite useless,
Experiments succeed and experiments fail,
Like everything else in this world,
  in which the truth advances
  like some splendid silver bulldozer
  in the tumbling darkness.

Miroslav Holub.

To my parents.

COMPLEX CHEMISTRY OF TRANSITIONAL METALS WITH THE TRIMETHYLSILYLMETHYL FUNCTION.

INTRODUCTION.

In the past, it has been generally accepted that the transition metal to carbon bond in simple alkyl and aryl complexes is weak since many metal-organo compounds have low thermal stability [1]. Increased stability may be obtained by the presence of π-accepting ligands, particularly for square-planar nickel, palladium and platinum complexes [2]. However, recent work suggests that the transition metal to carbon bond is no weaker than bonds between carbon and other metallic elements, and supporting ligands are not always necessary [3-6]. Evidence for the stability of transition metal alkyl bonds and the role of supporting ligands has recently been compiled [7].

There is a lack of direct thermodynamic evidence on the strength of transition metal-carbon bonds, but the data obtained suggest that these bonds are strong and do not differ from main group metal to carbon bonds or from those where the transition metal is bonded to hydrogen, oxygen, nitrogen or another metal. Thus the titanium-carbon force constant in tetramethyltitanium is very similar to the tin-carbon force constant in tetramethyltin [8]. Platinum-carbon bond lengths in alkyl compounds such as $(Me_3PtOH)_4$ [9], $(Et_3PtCl)_4$ [10], and <u>trans</u>-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$ [11] are all <u>ca</u> 2.10 Å and thus very close to the bond distance in $K[(acac)ClPtCHAc_2]$ [12] which is 2.11 Å. The metal-carbon stretching frequencies of these and other tertiary phosphine and arsine platinum complexes [13-15] all come in a narrow range, <u>ca</u>. 550 cm^{-1}, comparable to the range for main-group metal alkyl complexes. Tetraneopentyl chromium, $Cr(CH_2CMe_3)_4$ [5] has a comparable stability and similar physical properties to the alkoxide, $Cr(OEt)_4$ [16] and

the dialkylamide, $Cr(NEt_2)_4$ [17].

However, many transition metal-organo compounds have a higher lability than most main-group complexes. Tetramethyltitanium decomposes at -40°C in diethyl ether to give methane [8], but tetramethyltin is quite stable at room temperature. Such occurrences were explained in the past as a result of the weakness of the metal-carbon bond. It was suggested [2] that perhaps electrons were easily promoted from a relatively high energy, filled d orbital into an antibonding σ-orbital of the metal-carbon bond, or if the d orbital was empty, promotion occurred from the metal-carbon bonding orbital to a d orbital, thus weakening the metal-carbon bond. The crucial factor was the energy difference (ΔE) between the highest energy orbital containing electrons and the lowest energy vacant orbital. Since transition metal complexes have d orbitals which are rather close in energy, it was believed to be difficult to attain a ΔE greater than the minimum required for stability. In arguments particularly dealing with square-planar nickel, palladium and platinum complexes, Chatt and Shaw [2] discussed various ways of increasing ΔE and hence lessening the possibility of a homolytic dissociation occurring as described.

An increase in atomic number in a group of metals increases the interaction of the metal $d_{x^2-y^2}$ orbital and the ligand orbitals and increases ΔE, partly accounting for the observed increase in thermal stability of organo complexes in the order Pt > Pd > Ni.

π-Bonding ligands in the complex also increase ΔE since molecular orbitals of lower energy are formed by the bonding interaction of the d_{xy}, d_{xz} and d_{yz} metal orbitals with the ligand orbitals. If the ligand itself can form π-bonds, a further increase in stability is attained, as shown by the order of thermal stability

of complexes, L_2MR_2, where R = alkynyl> aryl> alkyl, i.e. in the order of decreasing π-bonding ability of the organic ligand.

A decrease in electronegativity of the ligand also increases ΔE by increasing the degree of π-bonding between the metal and the ligand, although a simultaneous decrease in the metal-ligand σ-bond strength opposes this effect.

Some of these widely-accepted arguments however, now need revision. The great variety of supporting ligands used to stabilise complexes [1] and the ever increasing number of isolable binary alkyl compounds containing no such ligands [3-6] implies that the electronic properties of the ligands are unimportant in altering the strength of the metal-carbon bond. Their presence does not guarantee stability, as shown by the derivatives of the complex, $RhH(CO)(PPh_3)_3$ whose use in catalysis depends on the instability of the metal-carbon bond [18]. Even ligands such as ammonia and water can give stable alkyl complexes [19], provided the species are inert to substitution, such as those of Cr(III), Co(III) and Rh(III). Thus it seems more likely that the main function of the ligands is to block coordination sites on the metal and hence prevent various types of dissociation process occurring. The role of supporting ligands is therefore not as important as had previously been believed.

Braterman and Cross [7] have further modified or refuted the old theories. They classify pathways for the cleavage of metal-carbon bonds as -

i) concerted - with more than one coordination site at the metal being involved,

ii) non-concerted promotional - when only one coordination site is involved and when the metal adopts an electronic configuration distinct from that assigned to it in the original complex, and

iii) non-concerted non-promotional - when only one coordination site is involved and the metal retains the same electronic configuration it had in the original complex.

A non-concerted promotional cleavage mechanism as put forward by Chatt and Shaw [2], is considered possible for metals at the start of the transition series, i.e. with less than six d electrons. A cleavage which produces radicals would place the unpaired electron of the metal-containing fragment in an orbital which is non-bonding with respect to the remaining metal-carbon linkages, and is of lower energy than that involved in the broken metal-carbon bond. This type of cleavage involves oxidation of the ligand from a formally anionic state R^- to a radical $R^\bullet$, with a corresponding reduction of the metal. This may perhaps be exemplified by the decomposition of $(CD_3)_3Cr(THF)_3$ to give CD_3H [20]. π-Donating ligands will inhibit this type of reaction by reducing the electron demand of the metal as in $(\pi\text{-}C_5H_5)_2TiMe_2$ [21] and $[(CH_3)_3SiCH_2]_3VO$ [3,4] which are relatively stable compounds. π-Accepting ligands would be effective only as good σ-donors in inhibiting the cleavage.

A non-concerted non-promotional cleavage giving radicals would put the unpaired electron of the metal-containing fragment in orbitals of the same symmetry as in the original compound. These excited states weaken the metal-carbon bond, but will not make thermal cleavage occur more readily.

For metals at the end of the transition series with six or more d electrons, a promotional process will involve excitation of a non-bonding electron to anti-bonding levels, as discussed by Chatt and Shaw[2]. For the square planar d^8 system, anion loss could proceed by a non-promotional cleavage giving a diamagnetic T-shaped species with the same electronic configuration as the original

complex, or by a promotional cleavage giving a trigonal species with a triplet ground state, corresponding to an excited state of the original.

However, metals of the second and third transition series usually undergo distortions to remove orbital degeneracies leading to triplet states, as shown by the non-existence of paramagnetic Pd(II) and Pt(II) complexes. A promotion can also only occur when the bond is already broken. This is because a large energy would be required for this to occur whilst the crystal field of the departing anion was appreciable. Some stabilisation of the promoted state however, would occur through electron-electron repulsion. These arguments thus seem to oppose the promotional mechanism suggested by Chatt and Shaw [2].

Radical and cation losses generating $\underline{d}^9$ and $\underline{d}^{10}$ species are non-promotional since their electronic configurations correlate with the ground state of the original complex. Similar arguments have been put forward for the $\underline{d}^6$ complexes [7].

Thus non-concerted ligand cleavage in $\underline{d}^6$ - $\underline{d}^9$ complexes must occur by a non-promotional mechanism, and is in fact comparable to the same process in main-group derivatives. Therefore in order to explain the greater lability of the transition metal alkyl complexes despite similar strengths of metal-carbon bonds, an alternative process, the concerted decomposition mechanism, must be postulated.

Three main types of concerted bond cleavage may be put forward; reductive elimination, binuclear elimination and β-elimination. Reductive elimination is the reverse process to oxidative addition and may be exemplified by the following reactions -

$$Me_3AuPPh_3 \longrightarrow MeAuPPh_3 + C_2H_6 \quad [22]$$

$$(Me_2PhP)_2PtMeCl_3 \longrightarrow (Me_2PhP)_2PtCl_2 + MeCl \quad [23]$$

Binuclear elimination is an intermolecular process involving the formation of metal-metal bonds and / or of metal-alkyl bridges. Such bridges are present in the ground state of beryllium and magnesium alkyls, and account for the ready exchange of alkyl groups in compounds of zinc, cadmium and mercury [24]. The final and probably the most important decomposition process is β-elimination -

$$\underline{L_nMCH_2CH_2R} \rightleftharpoons \underline{L_nM}\text{–}\underset{CHR}{\overset{H}{\overset{\|}{CH_2}}} \longrightarrow L_nMH + CH_2{=}\,CHR$$

as exemplified by the following:

$$LCuCH_2CD_2C_2H_5 \longrightarrow LCuD + CH_2{=}\,CD.C_2H_5 \quad [25]$$

$$R_2FeCH_2CD_2CH_2CH_2Ph \xrightarrow{\Delta} R_2FeD + CH_2{=}\,CD.CH_2CH_2Ph \quad [26]$$

However this type of reaction may be inhibited if -

a) the β-carbon atom (if present) of the alkyl chain bears no hydrogen or group of atoms which is as readily transferable as hydrogen,

b) there is a group of type $M.CH_2.XHR_n$ where X is any atom that can form a single but not a multiple bond to carbon,

c) there is a group whose chemistry forbids the formation of a double bond between the α and β-carbon atoms, or

d) the alkyl groups are fixed in such a configuration as to prevent ready transfer of atoms, such as hydrogen, to the metal.

The importance of a), that is, the absence of a β-hydrogen is shown by the studies of Tamura and Kochi [27] on the relative stabilities of dialkyl manganese compounds, prepared <u>in situ</u>, showing the order -

$Me \sim PhCH_2 \sim Me_3CCH_2 \gg Pr^n$, $Bu^n > Et > Bu^t > Pr^i$.

This is further borne out by the relative stabilities of recently isolated compounds such as tetramethyl titanium [28], hexamethyl tungsten [29], the benzyls of titanium, zirconium and vanadium [30,31], and the neopentyls of chromium, titanium and zirconium [5].

Condition b) could be fulfilled by the use of a variety of groups such as CH_2SnR_3, $CH_2Mn(CO)_5$, $C[B(OMe)_2]_3$ and, of particular interest, the trimethylsilylmethyl group, CH_2SiMe_3, which also fulfills condition a). A large number of new compounds have been isolated using this group [3,4,6,32], and the following discussion deals mainly with such compounds.

Condition c) is illustrated by the stable phenyl compounds, such as tetraphenyl titanium [33] which does not undergo β-elimination since this would lead to a thermodynamically unstable benzyne derivative. Complexes of fused alicyclic ring systems with a bridgehead-carbon, such as the stable compounds, tetrakis(1-norbornyl)-titanium, vanadium and chromium [34] are also stable to β-elimination according to Bredt's rule, which does not permit sp^2 hybridisation of a bridgehead-carbon. σ-Cyclopentadienyl complexes, such as the relatively stable compounds, $(\pi\text{-}C_5H_5)Mo(\sigma\text{-}C_5H_5)_3$ [35] and $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$ [21], also fall into this category since β-elimination would give rise to an allene linkage which is not found in rings which are less than 8-membered.

Condition d) may be upheld by using chelating alkyl ligands as in the stable compound, tris(ω-(dimethylarsino)-σ-tolyl)chromium(III), recently prepared [36], or by using bridging alkyl ligands as in the stable compounds, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_n$ where n is 3, 4, 5 and 6 [37]. Examples of stabilisation of alkyls in this way will be discussed later.

Thus it may be concluded that the transition metal-carbon bond is not inherently weak, supporting ligands are only of secondary importance in stabilising complexes, and new concerted cleavage mechanisms must be postulated for decomposition in place of the traditionally accepted promotional non-concerted mechanisms [1,2]. By using alkyl groups whose structures inhibit these concerted cleavage processes, a wide range of new alkyl complexes has been investigated.

RESULTS AND DISCUSSION.

It has been shown [3,4,6] that many transition metals can form stable alkyl complexes of the type MR_n where R is the trimethylsilylmethyl group. The stability of these complexes can partly be attributed to the inability of the ligands to eliminate a β-hydrogen and form an alkene. The bulkiness of the group may also increase the stability by blocking some concerted decomposition routes. Further increase in stability may also be given by some delocalisation of $d\pi$ electrons from the metal on to the silicon via $d\pi \rightarrow d\pi$ bonding. An analogous interaction between silicon and its β-atoms has been observed in e.s.r. measurements on silylalkyl radicals [38].

In order to provide a comparison with the binary transition metal alkyl complexes mentioned previously, a number of representative types of compound containing the trimethylsilylmethyl group and π-bonding ligands have been prepared [32]. Despite the secondary role such supporting ligands are believed to play, as was discussed previously, the ligands appear to enhance the stabilities of the particular complexes prepared. The trimethylsilylmethyl complexes of platinum, palladium, gold, cobalt, manganese, and titanium have been obtained, and neopentyl complexes of platinum and gold have also been prepared as a comparison for the discussion of the stabilities of these compounds.

PLATINUM COMPLEXES.

Platinum alkyl compounds are amongst the most stable σ-bonded organo-transition metal complexes known, both in thermal and oxidative stability. Methyl derivatives of platinum (IV) have been known since 1907 [9,39], but the first platinum (II) alkyl compounds were not reported till over fifty years later [2a,13]. For phosphine complexes, Chatt and Shaw observed that the stability decreased in the alkyl derivatives as the series Me, Et, n-Pr, n-Bu and benzyl was ascended [40]. With pyridine or alkene ligands, such as 1,5-cyclo-octadiene, only the methyl derivatives were easily isolated [41]. However, using the trimethylsilylmethyl ligand, quite stable, readily isolable compounds may be prepared.

The complex, cis-$PtCl_2(PMe_2Ph)_2$, reacted with trimethylsilyl-methyl-lithium, LiR, to give cis-$PtR_2(PMe_2Ph)_2$. This was a colourless, crystalline solid which was stable in air for several weeks and decomposed only slowly in hydrocarbon solvents. The ^1H nuclear magnetic resonance of the three methyls of the trimethylsilylmethyl group consisted of a singlet at τ 9.72. The methylene showed a doublet centred at τ 9.20, due to splitting by ^{31}P of nuclear spin one half and 100% abundance. The doublet had doublet satellites on each side due to the splitting by the ^{195}Pt isotope of nuclear spin one half, which occurs naturally in 34% abundance. The three sets of doublets were roughly in the ratio 1:4:1 for this reason, although one set of satellite doublets was hidden under the resonance of the dimethyl-phenylphosphine groups. The coupling constants for the methylene group were $J(^{195}Pt\text{-}H)$ = 76 Hz and J(P-H) = 4.5 Hz. The methyls of the dimethylphenylphosphine groups showed a resonance pattern consisting of a doublet at τ 8.80, also with ^{195}Pt satellites. The coupling constants were $J(^{195}Pt\text{-}H)$ = 20 Hz and J(P-H) = 7.8 Hz. The phenyls of

the phosphine occurred at τ 2.70, under the resonance signal due to benzene, which was used as the solvent. The n.m.r. is shown in Spectrum 1.

The doublet pattern of the methyls of the dimethylphenylphosphine is an indication that the stereochemistry of the complex, $PtR_2(PMe_2Ph)_2$, is in fact cis. In a trans compound, 'virtual' coupling [42] of the two phosphorus atoms occurs, giving rise to a triplet pattern. The coupling constant J(P-H) lies within the limits J(P-H) = 7- 13 Hz quoted by Jenkins and Shaw [42] for cis dimethylphenylphosphine complexes.

The infra-red spectrum of cis-$PtR_2(PMe_2Ph)_2$ showed the characteristic groups of bands assignable to the $SiMe_3$ group vibrations. The bands [4] appear at nearly identical positions for binary alkyls and those with π-bonding ligands, and show that the $SiMe_3$ group can be considered as an independent vibrating system. The characteristic bands appear at:

i) ca. 3000 - 2900 cm^{-1}, weak bands due to C-H stretches of $-CH_3$ and, overlapping, $-CH_2-$;

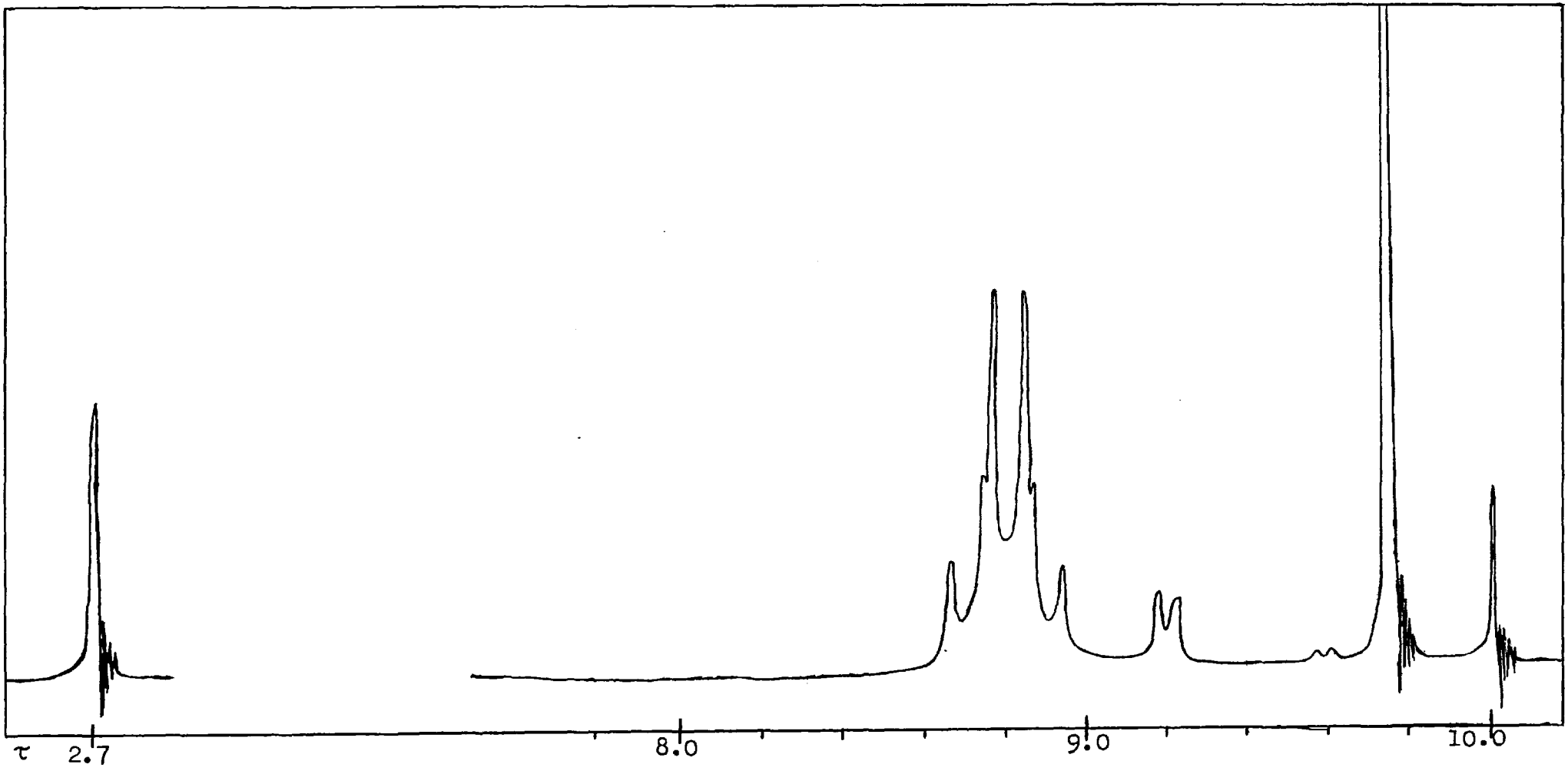
ii) ca. 1400 - 1460 cm^{-1}, several medium to weak bands overlapping to some extent, assignable as CH_3 deformations. The in-plane deformations of the $-CH_2-$ groups also occur here.

iii) ca. 1260 - 1230 cm^{-1}, all spectra showing two strong sharp peaks. This appears to be the characteristic [43] symmetric deformation of CH_3-Si which in the Me_3Si group has two components of unequal intensity.

iv) ca. 950 - 800 cm^{-1}, strong i.r. bands arising from methyl rocking vibrations probably coupled with Si-C stretches.

There are also bands in the region ca. 1200 - 950 cm^{-1} which appear to be sensitive to the nature of X in XCH_2SiMe_3. These are fundamentals involving mainly the various $-CH_2-$ angular movements, predominantly wagging and twisting.

N.m.r. spectrum of <u>cis</u>-$Pt(CH_2Si(CH_3)_3)_2(PMe_2Ph)_2$. (Benzene solution, T.M.S. internal reference.)



Spectrum 1.

The frequencies of the symmetric deformations of CH_3-Si and the methyl rocking vibrations coupled with Si-C stretches for *cis*-$PtR_2(PMe_2Ph)_2$ and the other compounds prepared are given in Table 1. These two sets of frequencies were used to characterise the trimethylsilylmethyl complexes. The platinum-carbon stretching frequencies are also given, and are observed to be very close to the frequencies found in other platinum alkyl complexes [13,14]. Very great difficulty in obtaining Raman spectra was experienced due to decomposition in the beam.

Some oxidative additions were attempted with *cis*-$PtR_2(PMe_2Ph)_2$. The complex was dissolved in methyl iodide and left in the dark for three days. Very pale yellow crystals were obtained, but microanalysis and a melting point determination showed the product to be $[PtI_2Me_2(PMe_2Ph)_2]$ (Figure 1).

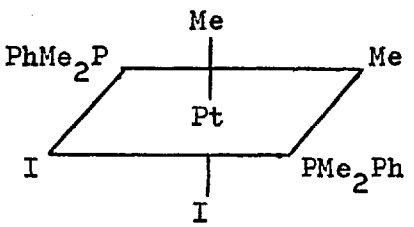


Figure 1.

This structure was confirmed by the n.m.r. spectrum [14] which showed a triplet at τ 9.13 with ^{195}Pt satellites (J(Pt-H) = 67 Hz, J(P-H) = 5.6 Hz) due to the methyl groups, both equivalent and split by the two phosphorus atoms *cis* to them, and a triplet at τ 7.47 with ^{195}Pt satellites (J(Pt-H) = 19.5 Hz, J(P-H) = 7.8 Hz) due to the methyls of the dimethylphenylphosphines. This triplet arises because of 'virtual' coupling by the two phosphorus atoms, since the phosphine groups are now in a *trans* configuration [42]. No evidence for the presence of trimethylsilylmethyl groups was found either in the n.m.r. or i.r. spectra. Thus the *cis*-trimethylsilylmethyl groups were

Table 1.

I.r. spectra of trimethylsilylmethyl (R) and neopentyl (np) complexes of platinum [a].

Compound	$\delta_{sym}(CH_3\text{-}Si)$ (cm^{-1})	$\upsilon(Si\text{-}CH_3)$ (cm^{-1})	$\upsilon(Pt\text{-}C)$ (cm^{-1})
cis-$PtR_2(PMe_2Ph)_2$	1247, 1235	850, 825	522
cis-$PtR_2(PPh_3)_2$	1249, 1235	844, 826	
cis-$PtR_2(AsPh_3)_2$	1246, 1235	852,848,825	518, 512
trans-$PtRCl(AsPh_3)_2$	1260, 1235	845,822,800	520, 510
PtR_2(1,5-COD)	1248, 1236	842, 821	560w[b],540sh,533s
PtR_2(bipy)	1260, 1251sh	848, 821	552
	1242, 1235	802	
$Pt_3R_6(SMe_2)_3$	1251, 1239	848, 822	542
trans-$PtHR(PEt_3)_2$[c]	1243, 1231	846, 815	
cis-$Pt(np)_2(PMe_2Ph)_2$	1236, 1230		

a) As Nujol mulls, KBr plates.

b) Raman spectrum on solid gave bands at 562w, 544s cm^{-1}.

c) $\upsilon(Pt\text{-}H)$ = 1955 cm^{-1}.

displaced by methyl iodide, probably to give trans-$PtIMe(PMe_2Ph)_2$, to which a trans addition of methyl iodide occurred, giving the product, $[PtI_2Me_2(PMe_2Ph)_2]$. Such an isomerisation is to be expected since the equilibrium between compounds such as cis and trans-$PtX_2(PY_3)_2$, where X is halogen, Y is hydrocarbon, shifts towards the trans side when the halogen is iodine and when Y is an alkyl group [44].

With acetylbromide, cis-$PtR_2(PMe_2Ph)_2$ gave an immediate white precipitate of the dibromo complex, cis-$PtBr_2(PMe_2Ph)_2$, identified by its infra-red spectrum and a melting point determination. No reaction at all was obtained with trifluoromethyliodide and the dialkyl. Thus cis-$PtR_2(PMe_2Ph)_2$ does not appear to undergo oxidative additions very readily, probably because the trimethylsilylmethyl groups are too bulky to give a stable platinum (IV) complex. Similar displacements of bulky groups have been observed with methyl iodide, as in the following reactions -

$$(Ph_3P)_2Pt(\sigma\text{-tolyl})_2 + MeI \xrightarrow{115^\circ} (Ph_3P)_2PtCH_3I_3 \quad [41]$$

$$(COD)Pt(\sigma\text{-tolyl})_2 + MeI \xrightarrow{115^\circ} (COD)Pt(\sigma\text{-tolyl})I \quad [41]$$

Platinum (IV) alkyl complexes prepared to date have mostly been methyl derivatives [9,14].

cis-$PtCl_2(PPh_3)_2$ reacted with the trimethylsilylmethyllithium, LiR, to give cis-$PtR_2(PPh_3)_2$, a colourless, crystalline, very stable solid. The n.m.r. spectrum showed a singlet at τ 9.67 due to the methyls of the ligand and a doublet at τ 8.88 with ^{195}Pt satellites, (J(Pt-H) = 85 Hz, J(P-H) = 4.8 Hz), due to the resonance of the methylene group. The compound showed the characteristic peaks in the i.r. spectrum.

cis-$PtCl_2(AsPh_3)_2$ gave two products with trimethylsilylmethyllithium, LiR. The major product was the dialkyl, cis-$PtR_2(AsPh_3)_2$, which was also the sole product when the reaction mixture was heated under reflux in benzene, and the minor product was the monoalkyl,

trans-$PtRCl(AsPh_3)_2$. The dialkyl, cis-$PtR_2(AsPh_3)_2$, was isolated as stable, colourless crystals, giving characteristic peaks in the i.r. spectrum. The n.m.r. showed a singlet for the methyls at τ 9.65 and a singlet at τ 8.65 with platinum satellites, (J(Pt-H) = 93 Hz), for the methylene resonance. The monoalkyl, trans-$PtRCl(AsPh_3)_2$, was isolated as pale brown crystals, the n.m.r. showing singlets at τ 10.19 and τ 9.28 for the methyl and methylene resonances, respectively, of the trimethylsilylmethyl group. The platinum-hydrogen coupling constant (J(Pt-H) = 115 Hz) was greater than that of the dialkyl and suggested that the compound was the trans-isomer. This was by analogy with the methyl compounds, cis-$PtMe_2(PMe_2Ph)_2$ and cis and trans-$PtMeCl(PMe_2Ph)_2$ whose platinum-hydrogen coupling constants are J(Pt-H) = 67, 56, and 82 Hz respectively [14]. Only the trans isomers of monoalkyl derivatives of other arsines have been isolated [15], since the isomerisation of the cis to the trans-isomer is very readily catalysed by traces of free arsine, which are very difficult to remove from a reaction mixture.

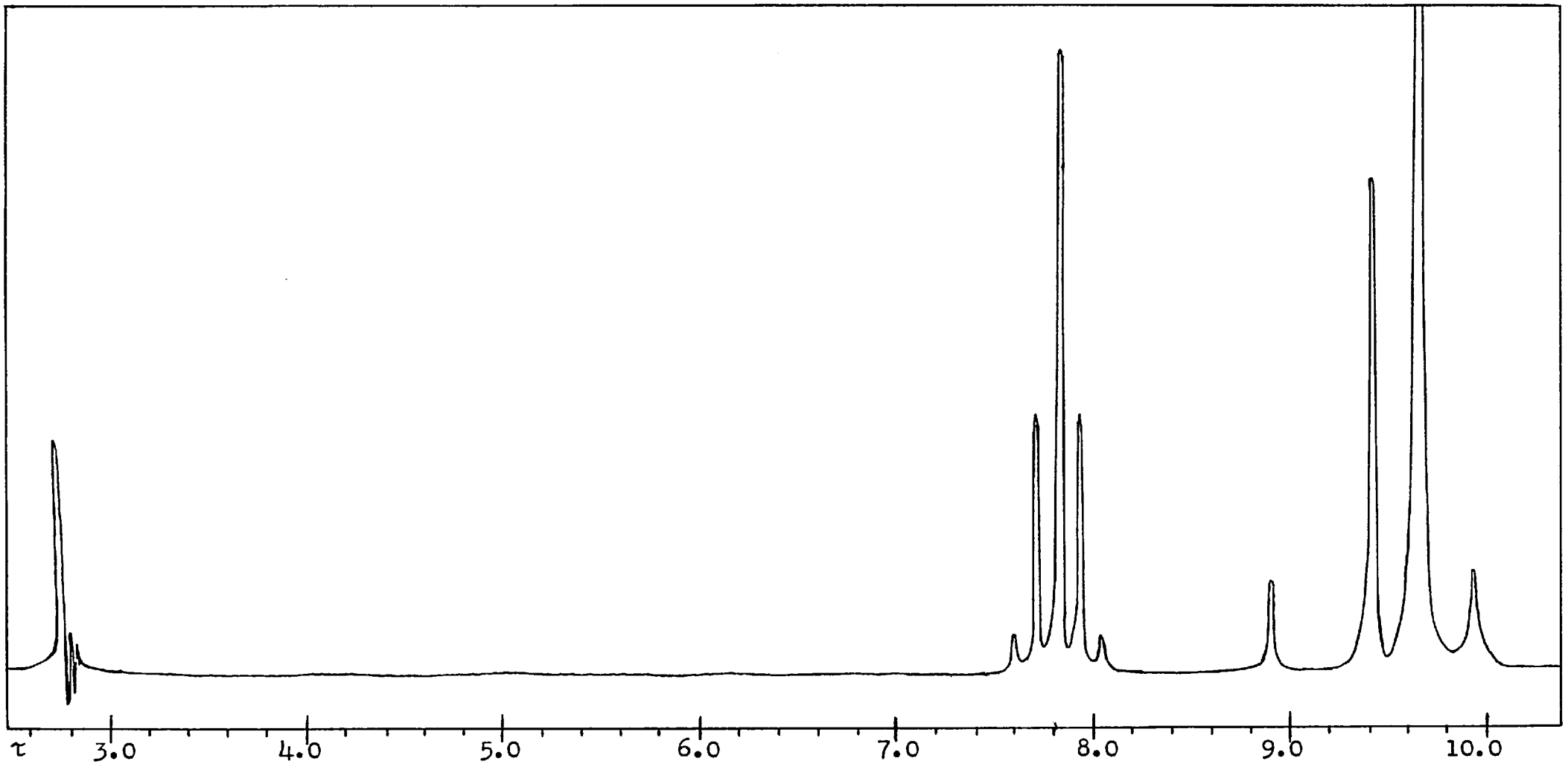
PtR_2(1,5-cyclo-octadiene), prepared from the corresponding dichloro compound with LiR, was a colourless, crystalline, stable solid. The methyl resonance of the trimethylsilylmethyl groups occurred as a singlet at τ 9.67 and the methylene resonance as a singlet at τ 8.82 with platinum satellites (J(Pt-H) = 95 Hz). The vinylic protons of the 1,5-cyclo-octadiene showed a broad singlet at τ 5.40 with platinum satellites (J(Pt-H) = 40 Hz), and the methylenes were observed as a multiplet at τ 8.12. The dimethyl analogue, $PtMe_2$(1,5-cyclo-octadiene) gave a broad singlet with platinum satellites (J(Pt-H) = 18 Hz) for the resonance of the cyclo-octadiene methylene protons [41]. However our multiplet could not be resolved to show a similar resonance pattern. A combination of fine proton-proton coupling and platinum splitting probably gave rise to the complex shape of the resonance. The characteristic

trimethylsilylmethyl peaks were observed in the infra-red spectrum. A Raman spectrum was also obtained on the solid sample, in the region of the platinum-carbon stretching frequencies (Table 1). The cyclo-octadiene derivative was the only compound prepared which did not immediately decompose in the laser beam.

PtR_2(2,2'-bipyridyl) was prepared as stable dark red crystals from the dichloro-2,2'-bipyridylplatinum complex with trimethylsilylmethyl-lithium. The n.m.r. showed a singlet at τ 9.52 for the methyls of the trimethylsilylmethyl groups and a singlet at τ 8.55 with platinum satellites (J(Pt-H) = 91 Hz) for the methylene group. The resonances of the 2,2'-bipyridyl group were hidden under the benzene signal from the solvent and were not investigated. The infra-red showed four peaks in the region of the symmetric deformation of CH_3-Si (Table 1), and these were probably due to the overlap of the characteristic two peaks of methyl-silyl groups with ring C-H deformations of the bipyridyl group which occur in the same region of the spectrum.

The dimethyl sulphide complex, cis-$PtCl_2(SMe_2)_2$, reacted with trimethylsilylmethyl- lithium to give, unexpectedly, a trimeric complex, $Pt_3R_6(SMe_2)_3$. This was formulated as having bridging sulphide groups. The complex was a white crystalline solid which was stable in air for several days, but solutions in benzene slowly darkened over a period of hours, losing dimethyl sulphide. The n.m.r. showed a singlet at τ 9.70 for the methyls of the trimethylsilylmethyl group and a singlet at τ 9.40 with platinum satellites (J(Pt-H) = 102 Hz) for the methylene resonance. The sulphide methyls occurred at τ 7.83 as a quintet of intensity ratios 1:8:18:8:1. This pattern arose from coupling with two adjacent equivalent platinum nuclei, (J(Pt-H) = 22 Hz), and hence suggested that the complex contained more than one platinum atom. The n.m.r. is shown in Spectrum 2. A molecular weight determination showed

N.m.r. spectrum of $Pt_3(CH_2Si(CH_3)_3)_6(SMe_2)_3$. (Benzene solution.)



Spectrum 2.

the compound to be a trimer. None of the expected product, cis-$PtR_2(Me_2S)_2$ was isolated. The sulphide methyls of this compound would have been observed as a singlet with platinum satellites, i.e. effectively as a 1:4:1 triplet.

Some dimeric haloplatinum complexes such as $Pt_2(Me_2S)_2Cl_4$ have been shown to have bridging sulphide groups [45] (Figure 2).

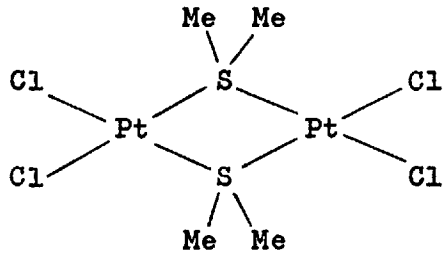


Figure 2.

The monobasic dialkyl sulphide group has one lone pair of electrons capable of interacting repulsively with non-bonded d electrons of the platinum metal. If this lone pair is accomodated in a bonding orbital with the metal as in the platinum dimers mentioned, the repulsion is eliminated and a shorter, stronger bond is produced. This same effect probably occurs in $Pt_3R_6(SMe_2)_3$, but it is not obvious why a trimer should be formed in preference to a dimer. Another compound containing a sulphide bridge is $[(CH_3)_2S]_3(CH_3)_4Rh(III)_2I_2$ [46] (Figure 3). The difference between the two sorts of sulphide was clearly shown in the n.m.r.

It is interesting to note that although a stable methyl derivative of a chelating sulphur ligand, viz $PtMe_2(EtSCH_2CH_2SEt)$, has been reported [2a], previous attempts to prepare alkyl complexes of platinum stabilised by monodentate sulphur ligands were unsuccessful, since the products decomposed in the work-up [47]. Stable aryls such as phenyl, o-tolyl and mesityl, were prepared

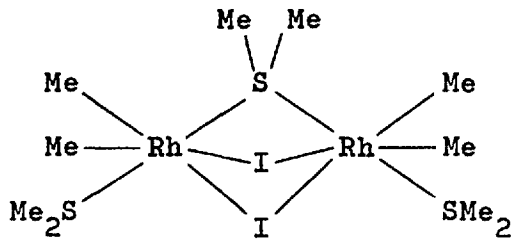


Figure 3.

with diethyl sulphide as ligand, to give cis and trans-$PtR_2(SEt_2)_2$[47]. It was suggested that stability was due to overlap of the filled 5d platinum orbitals with the aromatic π-orbitals, with the diethyl sulphide exerting an influence by inductive electron release to the platinum. Thus our compound, $Pt_3R_6(SMe_2)_3$, appears to be the first stable alkyl of platinum with monodentate sulphides, and it gains its stability by possessing dimethyl sulphide bridges in which lone pair repulsion from the sulphur atoms is eliminated.

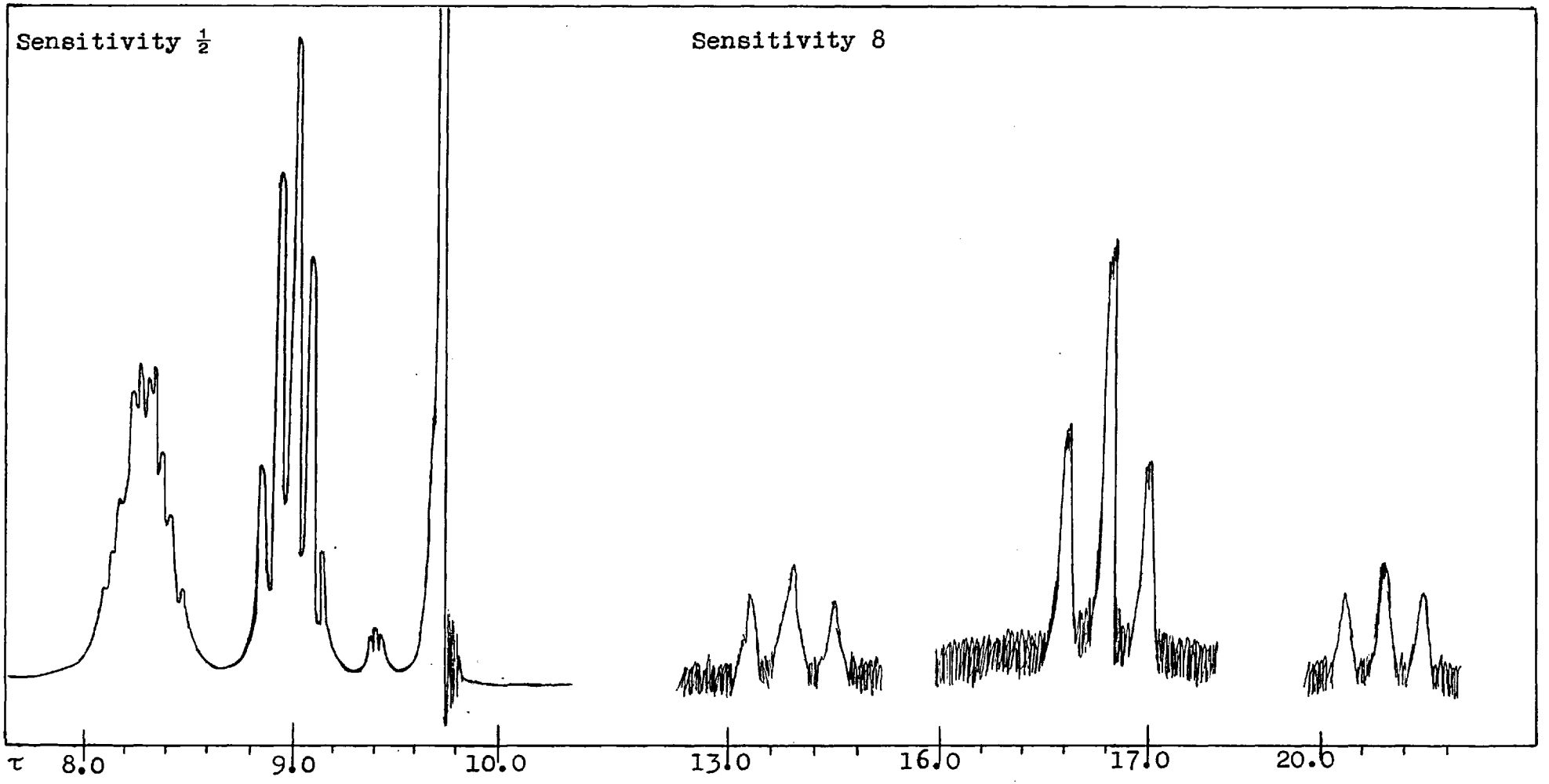
The dimethyl sulphide bridges however, were quite readily broken by triphenylphosphine and pyridine in benzene solutions to give cis-$PtR_2(PPh_3)_2$ and cis-$PtR_2(py)_2$ respectively and free dimethyl sulphide. cis-$PtR_2(PPh_3)_2$ showed an n.m.r. spectrum identical with that from the same compound prepared from cis-$PtCl_2(PPh_3)_2$ and trimethylsilylmethyl-lithium as described previously. cis-$PtR_2(py)_2$ showed a singlet at τ 9.75 due to the methyls of the trimethylsilylmethyl group and a singlet at τ 9.12 with platinum satellites, (J(Pt-H) = 90 Hz), for the methylene resonance. The compound was not isolated.

The pyridine compound could not be isolated from the reaction of cis-$PtCl_2(py)_2$ with LiR either. The reaction mixture slowly turned dark red when allowed to warm up to 0°C from -78°C, at which temperature the addition of the lithium reagent was made. A red oil was isolated which showed the characteristic peaks for trimethyl-

silylmethyl groups in the infra-red spectrum, but the n.m.r. showed a multitude of peaks between τ 9 - 10. Chromatography gave several fractions, but complexity in the n.m.r.was still observed for each fraction, and no pure products could be isolated.

The hydrido-alkyl complex, trans-$PtHR(PEt_3)_2$, has been prepared from trans-$PtHCl(PEt_3)_2$ and trimethylsilylmethyl-magnesium chloride. This was obtained as a stable, off-white, viscous oil which could not be freed completely from high-boiling impurities derived from the Grignard reagent. However the n.m.r. spectrum identified the compound satisfactorily. The methyl resonance of the trimethylsilylmethyl group occurred as a singlet at τ 9.70 and the methylene resonance occurred as a triplet, due to coupling with two phosphorus atoms, at τ 9.4. The signals due to coupling with phosphorus and platinum atoms were obscured by the resonances of the triethylphosphine groups, and the coupling constants could not therefore be obtained. The hydride showed a triplet at τ 16.82, due to coupling with two phosphorus atoms trans to each other, and triplet satellites due to coupling with platinum. The coupling constants were J(Pt-H) = 705 Hz and J(P-H) = 19.5 Hz. The methyls of the triethylphosphine groups occurred as a quintet of intensity ratios 1:4:6:4:1 centred at τ 9.02. This pattern arose from the triplet, due to coupling with the methylene protons, J = 8 Hz, being further coupled to two phosphorus atoms in a trans configuration, with coupling constant, $J_{obs.}$(P-H) = 8 Hz also. The methylenes of the phosphine groups showed a multiplet, centred at τ 8.28. The quintet pattern of the methyls of the phosphines indicated a trans configuration of phosphines since 'virtual' coupling of the two phosphorus atoms had occurred [48]. If the two phosphines had been cis, 'virtual' coupling would have been negligible and two triplets would have been observed. The n.m.r. is shown in Spectrum 3.

N.m.r. spectrum of <u>trans</u>-$PtH(CH_2Si(CH_3)_3)(PEt_3)_2$. (Benzene solution.)



Spectrum 3.

The i.r. showed the characteristic bands for the trimethylsilylmethyl group, and the stretching frequency of the platinum-hydrogen bond was observed at 1955 cm^{-1} (Table 1).

Attempts were made to prepare a mixed alkyl complex from trimethylplatinum iodide, $(Me_3PtI)_4$, and trimethylsilylmethyl-lithium. A pale brown oil was obtained which showed in the n.m.r. a singlet at τ 8.20 with platinum satellites, (J(Pt-H) = 78 Hz), due to the three methyl groups, a singlet at τ 9.69 due to methyls of the trimethylsilylmethyl group and a singlet at τ 9.52 due to the methylene of the R group. The platinum satellites for the methylene resonance were not observed. The intensity ratios indicated three ordinary methyl groups to one trimethylsilylmethyl group. The starting material, $(Me_3PtI)_4$, showed several peaks in the i.r. in the regions of the characteristic frequencies for the trimethyl-silylmethyl group. The mixed alkyl complex prepared showed some slight changes in the infra-red in these regions, but the overall spectrum was not outstandingly different. An analytically pure sample could not be isolated from the oily product.

Neopentyl-lithium, npLi, was reacted with several of the platinum chloro complexes used above in order to prepare trimethyl-methyl complexes and contrast them with the trimethylsilylmethyl compounds. cis-$Pt(np)_2(PMe_2Ph)_2$ was prepared from the corresponding chloro complex as a creamy-coloured solid, and was found to be of similar stability to the analogous trimethylsilylmethyl complex. The n.m.r. showed a singlet at τ 8.56 due to the methyls of the neopentyl group and a doublet at τ 7.76, due to coupling with the phosphorus atom, with platinum satellites for the methylene group. The coupling constants were J(P-H) = 6.5 Hz and J(Pt-H) = 78 Hz. The methyls of the dimethylphenylphosphine groups were observed as a doublet centred at τ 8.99 with platinum satellites, only half of

each doublet satellite being actually observed. The other half was hidden under the broad main doublet resonance. The coupling constants were J(P-H) = 7.5 Hz and J(Pt-H) = 14 Hz. The doublet pattern for the phosphine methyls indicated a cis stereochemistry for the phosphines [42], coupling only occurring with one phosphorus atom since 'virtual' coupling was negligible. The infra-red spectrum showed two sharp peaks in the 1260 - 1230 cm^{-1} region due to skeletal vibrations of the CH_3-C grouping. This is therefore coincident with the frequencies of the symmetric deformation of CH_3-Si and may be used as a characteristic for the neopentyl group. No strong characteristic peaks are observed in the 850 - 800 cm^{-1} region, whereas in trimethylsilylmethyl complexes the methyl rocking vibrations coupled with Si-C stretches produce strong intensity peaks in this region. In neopentyl complexes the methyl rocking vibrations are too weak to produce clear peaks of characteristic frequencies.

Attempts to prepare other neopentyl analogues were unsuccessful since pure compounds could not be isolated. However, some comparison may be made between the trimethylsilylmethyl and neopentyl dimethylphenylphosphine complexes. Not much difference in stability was observed between the two compounds. However the difference in chemical shift between the methylene proton resonances of cis-$PtR_2(PMe_2Ph)_2$ and cis-$Pt(np)_2(PMe_2Ph)_2$ was 1.44 p.p.m. (Table 2) whereas the corresponding difference in $(CH_3)_3SiCH_2Cl$ and $(CH_3)_3CCH_2Cl$ was only 0.52 p.p.m. This implies that there is a difference in the electronic environment of the methylene group in the two platinum complexes. The same sort of difference, 1.25 p.p.m. was observed between the gold complexes, $AuRPPh_3$ and $Au(np)PPh_3$, which will be discussed later.

E.s.r. measurements on silylalkyl radicals [38,49] show that an interaction occurs between silicon and its β-atoms in radicals

Table 2.

N.m.r. spectra of trimethylsilylmethyl (R) and neopentyl (np) complexes of platinum [a,b].

Compound	τ(Methyl)	τ(Methylene)	J(Pt-H)(Methylene)(Hz)
cis-$PtR_2(PMe_2Ph)_2$	9.72 (s)	9.20 (d)	76
cis-$PtR_2(PPh_3)_2$	9.67 (s)	8.88 (d)	85
cis-$PtR_2(AsPh_3)_2$	9.65 (s)	8.65 (s)	93
trans-$PtRCl(AsPh_3)_2$	10.19 (s)	9.28 (s)	115
PtR_2(1,5-COD)	9.67 (s)	8.82 (s)	95
PtR_2(bipy)	9.52 (s)	8.55 (s)	91
$Pt_3R_6(SMe_2)_3$	9.70 (s)	9.40 (s)	102
cis-$PtR_2(py)_2$ [c]	9.75 (s)	9.12 (s)	90
trans-$PtHR(PEt_3)_2$ [d]	9.70 (s)	9.40 (t)	*
$PtMe_3R$ [c]	9.69 (s)	9.52 (s)	*
cis-$Pt(np)_2(PMe_2Ph)_2$	8.56 (s)	7.76 (d)	85
RCl	10.01 (s)	7.46 (s)	
npCl	9.20 (s)	6.94 (s)	

a) All measurements made in benzene solutions at 100 MHz. τ values relative to benzene = τ 2.70.

b) s = singlet, d = doublet, t = triplet.

c) Compound not isolated.

d) Hydride τ 16.82 (t), J(Pt-H) = 705 Hz.

* Obscured by other resonances.

such as $(CH_3)_3SiCH_2CH_2^{\bullet}$. Delocalisation of the odd electron occurs on to the vacant d orbitals of the silicon atom. It is therefore reasonable to suppose that an analogous delocalisation may occur with $d\pi$ electrons of a metal in the β-position to silicon, as in trimethylsilylmethyl-platinum complexes. Such delocalisation via $d\pi \longrightarrow d\pi$ bonding is impossible in neopentyl complexes, and accounts for the difference in electronic environment of the two methylene groups and hence the difference in chemical shifts. The delocalisation also causes an increase in stability for trimethylsilylmethyl complexes compared to the corresponding neopentyl complexes, and this is demonstrated quite clearly in the sections on palladium and gold complexes.

The coupling constants, J(Pt-H), observed for the methylene protons of the trimethylsilylmethyl compounds discussed previously, are much higher, (Table 2), than those found for similar methyl complexes, e.g., cis-$PtMe_2(PMe_2Ph)_2$, 67 Hz [14], cis-$PtMe_2(AsMe_2Ph)_2$, 79 Hz [15], $PtMe_2(COD)$, 86 Hz [41]. The system is far from simple however, and is not susceptible at present to discussion. However, it may be noted that of the cis ligands involved, the one with the lowest trans effect, namely dimethyl sulphide, leads to the greatest coupling between platinum and the methylene protons. This is to be expected, since it has been shown [50] that in methylplatinum (II) complexes, J(Pt-H) for the methyl group increases as the trans-influence of the ligand decreases.

The hydrido-complex, trans-$PtHR(PEt_3)_2$, was prepared as a simple means of ascertaining the trans-influence of the trimethylsilylmethyl group, since several recent spectroscopic studies [51,52] have shown that there is a close correlation between J(Pt-H) for a hydride and the influence of the trans-ligand. For a series of complexes trans-$PtHL(PEt_3)_2$ where L is o, m, or p-substituted

benzoato or substituted acetato ligand, linear correlations have been found for several spectroscopic parameters, as given in the following expression [52] -

$$J(Pt\text{-}H) \propto \tau(Pt\text{-}H) \propto \upsilon(Pt\text{-}H) \propto A(Pt\text{-}H)^{-3}$$

where A is the metal-hydrogen distance.

The hydride, trans-$PtHR(PEt_3)_2$, shows a very low coupling constant to platinum, J(Pt-H) = 705 Hz, a low chemical shift (τ 16.8) and a low i.r. stretching frequency, υ(Pt-H) of 1955 cm^{-1}. Most trans-platinum-hydrido complexes have J(Pt-H) occurring in the range 1000 - 1370 Hz, τ(Pt-H) in the range 22.6 - 33.7, and ν(Pt-H) between 2100-2270 cm^{-1}, [52-54]. The low values for these parameters for the hydrido-alkyl complex indicate that the $(CH_3)_3SiCH_2$ ligand has a very high trans-influence. It is in fact comparable to that of the cyanide ion, as shown by the corresponding data for the cyanohydride, trans-$PtHCN(PEt_3)_2$:- J(Pt-H) = 778 Hz, τ(Pt-H) = 17.16, ν(Pt-H) = 2041 cm^{-1} [53,54]. The combined effects of the trans-influence, i.e. the tendency of the ligand to weaken the bond trans to it, and the delocalisation of non-bonding d electrons of platinum to vacant d orbitals of silicon in the trimethylsilylmethyl group, drastically lower the d-electron density around the hydride ligand and result in the very low chemical shift and low platinum-hydrogen stretching frequency.

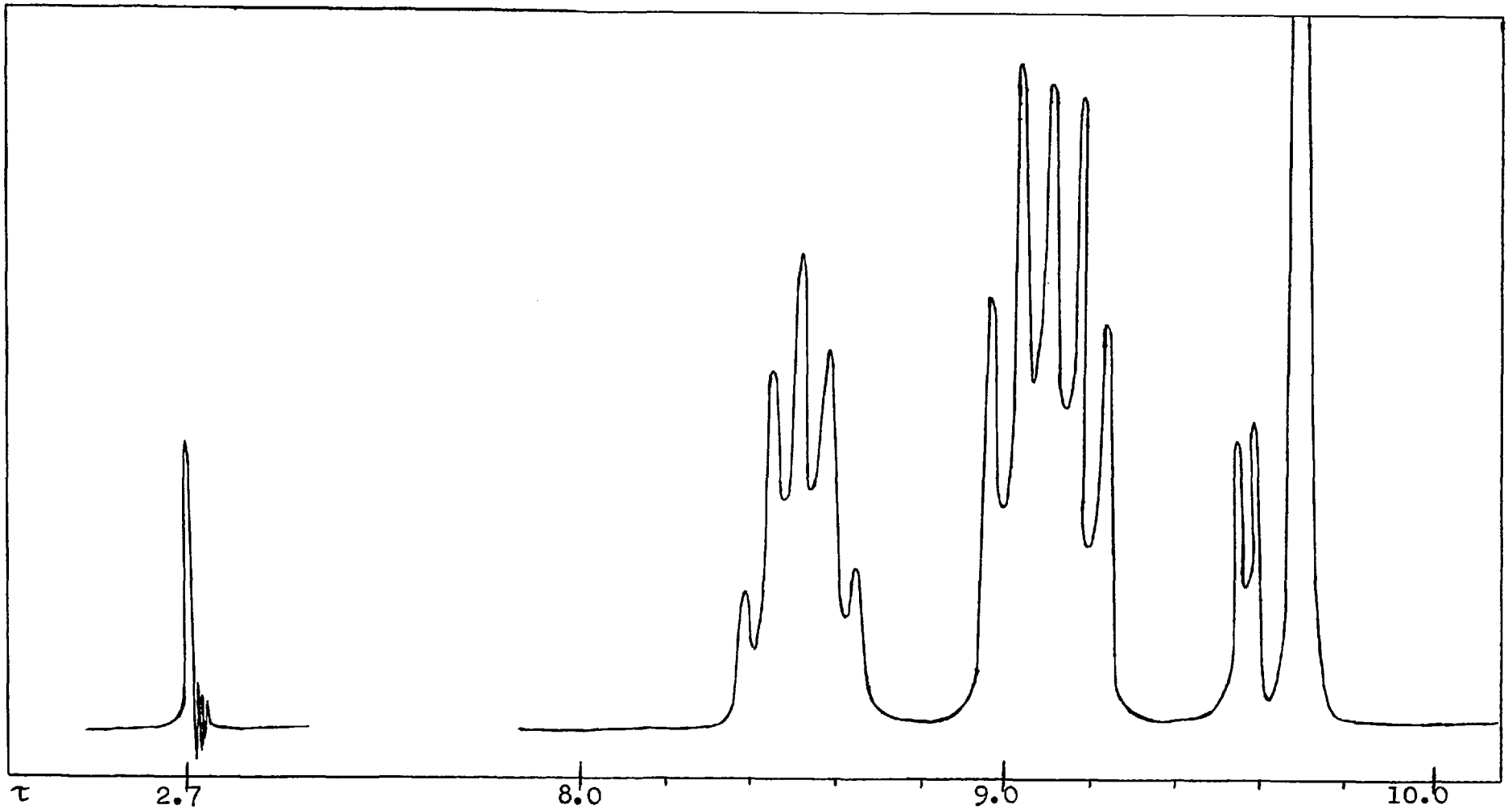
PALLADIUM COMPLEXES.

Organo-palladium compounds are generally less stable than their platinum analogues. While cis-$PdMe_2(PEt_3)_2$ is quite stable, the corresponding triphenylphosphine complex is not, and homologues higher than methyl are reported to be very unstable, even when triethylphosphine is the 'stabilising' ligand [55].

The trimethylsilylmethyl complex, cis-$PdR_2(PEt_3)_2$, was prepared from the corresponding dichloro complex and the lithium reagent LiR. It was isolated as pale yellow crystals which turned grey within a few hours and had decomposed after several days. The n.m.r. showed a singlet at τ 9.67 for the methyls of the trimethylsilylmethyl group, and a doublet at τ 9.54 due to the methylene resonance split by phosphorus, with coupling constant J(P-H) = 4 Hz. The methyls of the triethylphosphine gave a resonance centred at τ 9.08 with the pattern of a quintet of intensity ratios approximately 1:2:2:2:1. This was produced by the 1:2:1 triplet, due to coupling with the two methylene protons, (J = 7 Hz), being split by the phosphorus atom to form two overlapping triplets. The coupling constant J(P-H) was 14 Hz. These two triplets indicated that the phosphines were in a cis configuration, when 'virtual' coupling is negligible [48]. The methylenes of the triethylphosphine groups also gave a quintet pattern, but of intensity ratios 1:4:6:4:1, centred at τ 8.50. This was due to the 1:3:3:1 quartet, from coupling with the three methyl protons, (J = 7 Hz), being split by the phosphorus atom giving two overlapping quartets. The coupling constant J(P-H) was also 7 Hz. The n.m.r. is shown in Spectrum 4. The infra-red spectrum showed the characteristic peaks for trimethylsilylmethyl complexes (Table 3).

The mono-alkyl, trans-$PdRCl(PEt_3)_2$, was prepared from the cis-dichloro complex and trimethylsilylmethyl-magnesium chloride.

N.m.r. spectrum of <u>cis</u>-$Pd(CH_2Si(CH_3)_3)_2(PEt_3)_2$. (Benzene solution.)



Spectrum 4.

Table 3.

I.r. spectra of trimethylsilylmethyl (R) complexes of palladium [a].

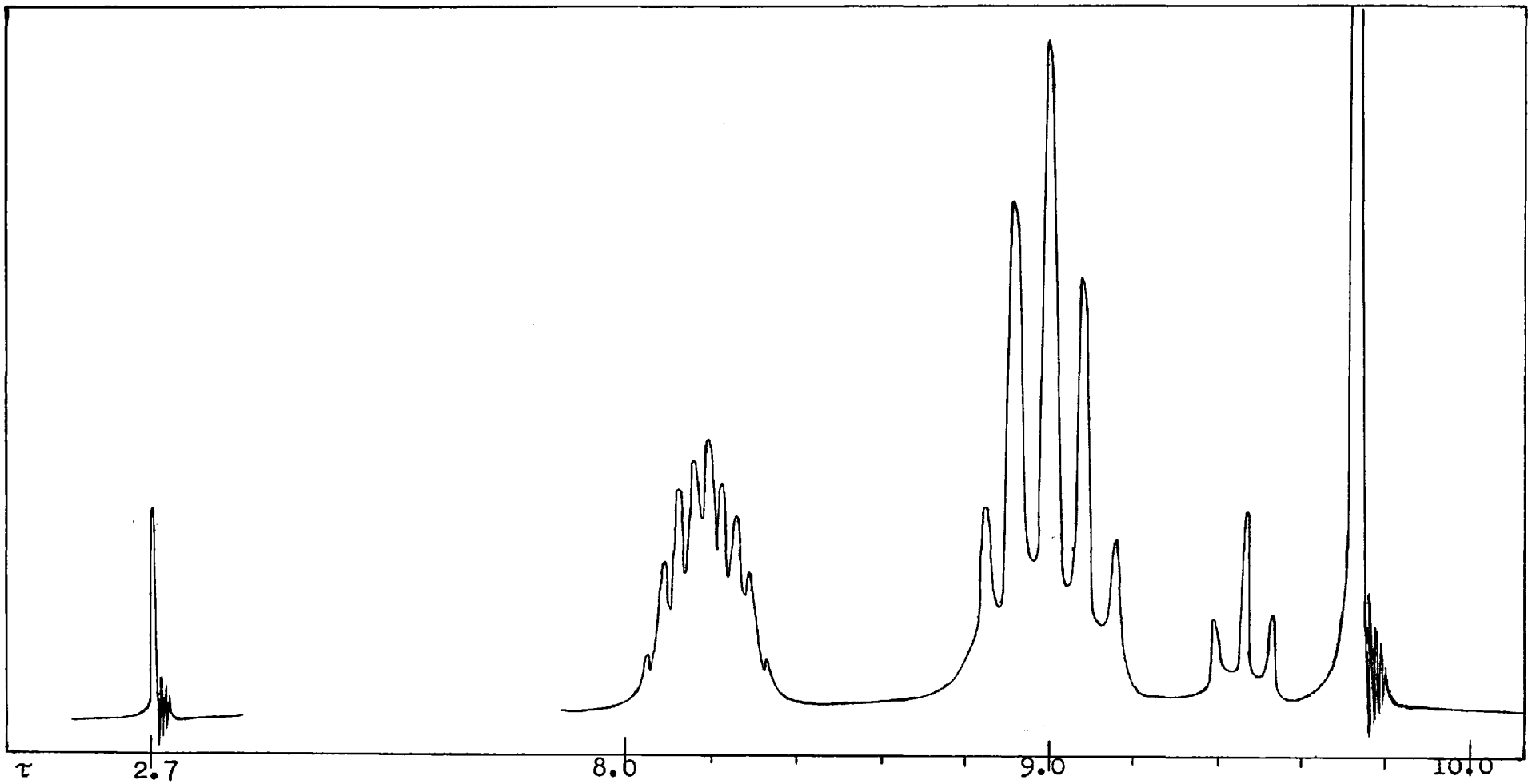
Compound	$\delta_{sym}(CH_3\text{-}Si)$ (cm^{-1})	$\nu(Si\text{-}CH_3)$ (cm^{-1})
cis-$PdR_2(PEt_3)_2$	1244, 1230	830
trans-$PdRCl(PEt_3)_2$	1272, 1245	830

a) As Nujol mulls, KBr plates.

It was a stable yellow, sublimable, sticky solid which could not be obtained analytically pure. However it was characterised satisfactorily by its n.m.r. spectrum. The methyls of the trimethylsilylmethyl group occurred as a singlet at τ 9.71 and the methylenes as a triplet, due to splitting by two phosphorus atoms cis to them, at τ 9.45, with coupling constant J(P-H) = 7 Hz. The methyls of the triethylphosphine groups occurred as a quintet of intensity ratios 1:4:6:4:1, centred at τ 9.00. The pattern was caused by the triplet due to the methylenes, J = 8 Hz, being split by the two phosphorus atoms which were 'virtually' coupled together since the phosphines were in a trans configuration [48]. The coupling constant $J_{obs.}(P\text{-}H)$ was also equal to 8 Hz. The methylenes of the triethylphosphines gave a multiplet centred at τ 8.18. The n.m.r. is illustrated in Spectrum 5. The characteristic peaks were observed in the infra-red spectrum (Table 3).

Attempts to prepare cis-$Pd(np)_2(PEt_3)_2$ gave a yellow-brown solid which was probably the required product, but it was not possible to purify it because it decomposed rapidly in solution. The increased stability of the trimethylsilylmethyl derivatives compared with neopentyl derivatives is thus very well illustrated

N.m.r. spectrum of <u>trans</u>-$Pd(CH_2Si(CH_3)_3)Cl(PEt_3)_2$. (Benzene solution.)



Spectrum 5.

here, and can be attributed to the delocalisation of $d\pi$ electrons from the metal on to the silicon atom *via* $d\pi \rightarrow d\pi$ bonding, as described previously.

Palladium mono-alkyls readily undergo insertion of carbon monoxide to give acyl derivatives [56]. *trans*-$PdRCl(PEt_3)_2$ reacted with carbon monoxide to give a yellow oily product whose infra-red showed a peak at 1640 cm^{-1}, *i.e.* in the correct region for acyls. This suggests that the product was probably *trans*-$Pd(COR)Cl(PEt_3)_2$, but the complex was not isolated. The dialkyl, *cis*-$PdR_2(PEt_3)_2$, gave with carbon monoxide a dark-red oily product which rapidly turned black in air. The i.r. showed a complex carbonyl pattern with terminal CO peaks at 2000, 1960 and 1940 cm^{-1} and bridging CO peaks at 1830 and 1805 cm^{-1}. The product was not characterised. This is closely analogous to the reaction of *cis*-$PdMe_2(PEt_3)_2$ with carbon monoxide, which gives an unstable orange-brown oil which also has a complicated carbonyl pattern in the i.r. [56].

Attempts to prepare other trimethylsilylmethyl complexes of palladium were unsuccessful.

GOLD COMPLEXES.

Gold forms compounds of the type (alkyl)$AuPPh_3$ [57]: the methyl and ethyl derivatives are stable, but the isobutyl derivative decomposes rapidly at room temperature [58].

The trimethylsilylmethyl derivative $RAuPPh_3$ has been isolated as very stable white crystals from the reaction of the chloro complex $ClAuPPh_3$ with LiR and also from the reaction of bromoauric acid with triphenylphosphine and the Grignard reagent RMgCl. The n.m.r. showed a singlet at τ 9.48 for the methyls of the trimethylsilylmethyl group and a doublet at τ 8.90 due to the methylene, split by one phosphorus atom, with J(P-H) = 10 Hz. The characteristic frequencies were observed in the infra-red (Table 4).

This complex was also reported by other workers [59] during our studies. Although our values for the melting point and the n.m.r. chemical shifts were in agreement with those given by Shiotani and Schmidbauer, we found $RAuPPh_3$ to be extremely stable, being unchanged in the solid for several months and stable in solution for several hours, whereas they observed it to be rather unstable. Their postulation [59] that a silicon atom in the β-position lowers over-all thermal stability is clearly untenable.

Furthermore, $ClAuPPh_3$ reacted with neopentyl-lithium to give (np)$AuPPh_3$ as an impure, beige solid which decomposed in solution more readily than the trimethylsilylmethyl compound, and decomposed on standing in air to a brown material. The n.m.r. showed a singlet at τ 8.37 due to the methyls of the neopentyl group and a doublet at τ 7.65 due to the methylene resonance split by phosphorus, (J(P-H) = 8 Hz). The characteristic frequencies for a neopentyl compound were observed in the infra-red (Table 4).

The reaction of bromoauric acid with methyldiphenylphosphine

Table 4.

I.r. spectra of trimethylsilylmethyl (R) and neopentyl (np) complexes of gold [a].

Compound	$\delta_{sym}(CH_3\text{-}Si)$	$\nu(Si\text{-}CH_3)$	$\nu(Au\text{-}C)$
$AuR(PPh_3)$	1239, 1232	856,844,825	529
$Au(np)(PPh_3)$	1260, 1238		528
$AuR(PMePh_2)$	1248, 1240	850, 845	
$(AuR_2Br)_2$	1256, 1245	840, 830	

a) As Nujol mulls, KBr plates, cm^{-1}.

and trimethylsilylmethyl-lithium gave $RAu(PMePh_2)$ as stable white crystals. The n.m.r. showed singlets at τ 9.48 and τ 9.05 for the methyl and methylene resonances respectively of the trimethylsilylmethyl ligand. The methylene resonance was rather broad and the splitting by phosphorus was not observed. The methyl of the methyldiphenylphosphine showed a doublet at τ 8.60, (J(P-H) = 15 Hz).

These compounds illustrate quite clearly the difference in stability between trimethylsilylmethyl and neopentyl complexes. The difference in chemical shift between the methylene proton resonances of the two triphenylphosphine compounds, 1.25 p.p.m. (Table 5), is much larger than the corresponding shift between $(CH_3)_3SiCH_2Cl$ and $(CH_3)_3CCH_2Cl$, 0.52 p.p.m. . This difference, agreeing with the analogous data for platinum complexes, may be ascribed to the delocalisation of $d\pi$ electrons from the metal on to the silicon atom. This effect causes an appreciable change in the electronic environment of the methylene protons in the trimethylsilylmethyl compound compared to that in the neopentyl

Table 5.

N.m.r. spectra of trimethylsilylmethyl (R) and neopentyl (np) complexes of gold [a,b].

Compound	τ(Methyl)	τ(Methylene)	J(P-H)(Methylene)
$AuR(PPh_3)$	9.48 (s)	8.90 (d)	10 Hz
$AuR(PPh_3)$[c]	10.08 (s)	9.82 (d)	10 Hz
$Au(np)(PPh_3)$	8.37 (s)	7.65 (d)	8 Hz
$AuR(PMePh_2)$	9.48 (s)	9.05 *	*
$(AuR_2Br)_2$	9.80 (s)	8.38 (s)	
RCl	10.01 (s)	7.46 (s)	
npCl	9.20 (s)	6.94 (s)	

a) All measurements made in benzene solutions at 100 MHz unless otherwise stated. τ values relative to benzene = τ 2.70.

b) s = singlet, d = doublet.

c) Dioxan solution.

* Broad peak, splitting by ^{31}P could not be resolved.

compound, and hence causes the large difference in chemical shifts for the methylenes in the two compounds. The delocalisation is also responsible for the increased stability of the trimethylsilyl-methyl complex compared to the neopentyl complex.

Bromoauric acid reacted with trimethylsilylmethyl-magnesium chloride in the cold and in the absence of light to give a brown solid, which rapidly blackened in air and on exposure to light. The n.m.r. spectrum showed singlets at τ 9.80 and τ 8.38 for the methyl and methylene resonances respectively of trimethylsilylmethyl groups and the infra-red showed characteristic peaks for these groups (Table 4). Comparison with analogous reactions with methyl and ethyl Grignards [57,60] suggests that the complex was the dimer $(R_2AuBr)_2$, with bridging bromide groups, but an analytically pure sample was not obtained. The neopentyl analogue, $(np_2AuBr)_2$ has been prepared in low yields (12%) by the same method [61]. All these dialkyl gold halides are unstable to heat and light, and the trimethylsilylmethyl analogue did not appear to possess any enhanced stability.

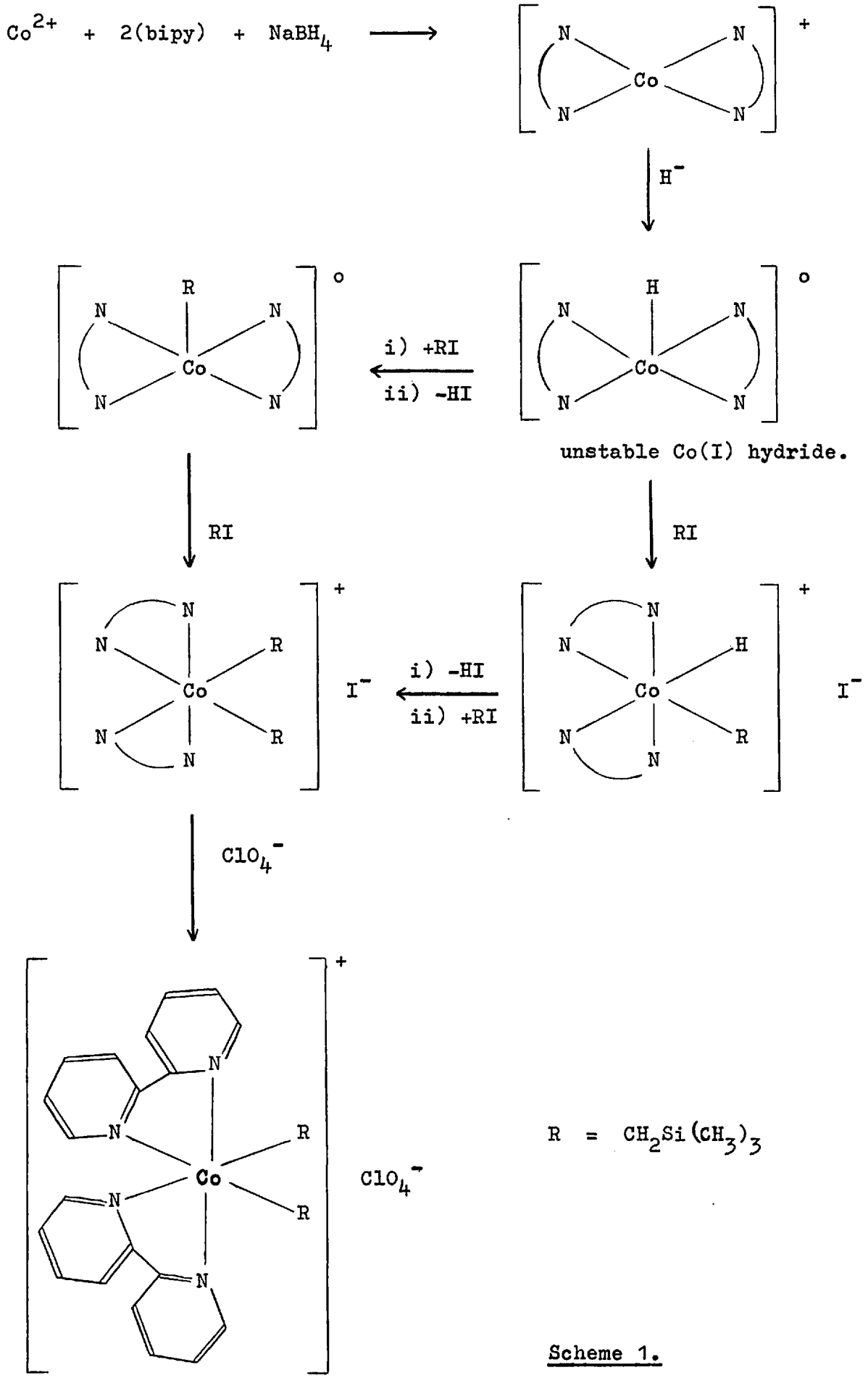
COBALT COMPLEX.

The methyl and ethyl cobalt (III) complexes, $[Co(alkyl)_2(bipy)_2]ClO_4$, are readily obtainable, but decompose slowly in air [62]. The trimethylsilylmethyl analogue, $[CoR_2(bipy)_2]ClO_4$, is a very stable compound, both in the solid state and in solution. It was obtained as a red, crystalline product from the reaction of cobalt (II) chloride, 2,2'-bipyridyl, sodium borohydride and iodomethyltrimethylsilane.

The borohydride reduces cobalt (II) to cobalt (I). This, when stabilised by polydentate, conjugated, chelating systems with nitrogen or oxygen as donor atoms, behaves as a powerful nucleophilic species and undergoes oxidative addition [62]. This is illustrated in the following mechanistic scheme for $[CoR_2(bipy)_2]ClO_4$ (Scheme 1).

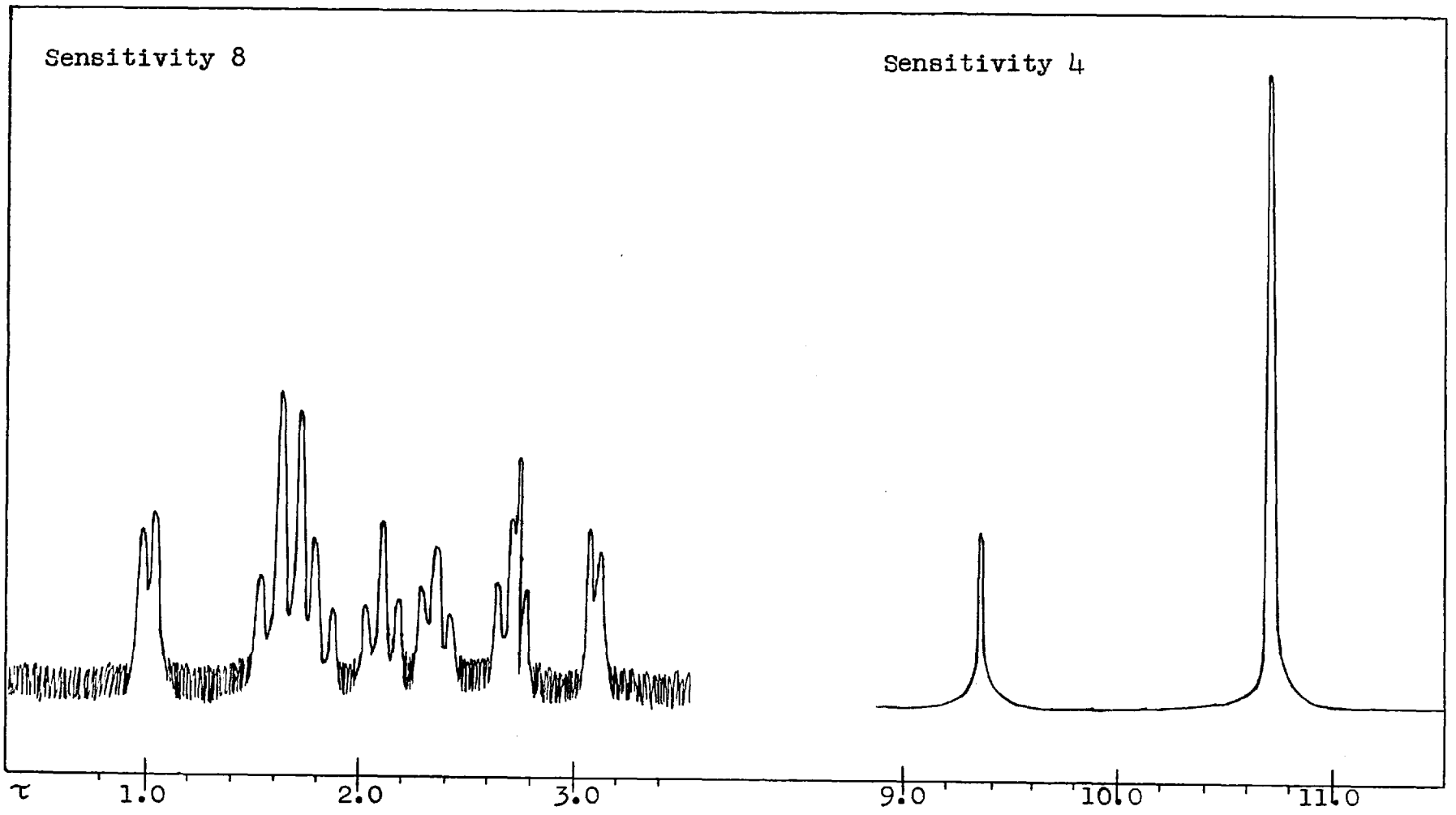
The n.m.r. showed singlets at τ 10.72 and τ 9.33 for the methyl and methylene resonances respectively of the trimethylsilylmethyl groups. The bipyridyl resonances occurred over the range τ 0.95 - 3.15. Four sets of triplets for the 4,5 and 4',5' protons were observed. The 3,3' protons gave two doublets which over-lapped with each other and with one of the triplets to give a complex pattern of five lines. The 6 and 6' protons appeared as doublets at τ 1.00 and τ 3.12 respectively. The 6'-proton lay close to and above the plane of the pyridine ring of the second ligand and experienced the pyridine ring current effect, and hence the high field shift was observed. The 6-proton did not feel this effect and was thus observed at the lower field. The n.m.r. is shown in Spectrum 6.

The n.m.r. showed that the compound was the cis-isomer since protons in equivalent positions in the bipyridyl rings were found to be non-equivalent in the n.m.r. spectrum. The trans-isomer


Co2+ + 2(bipy) + NaBH4
H-
i) +RI
ii) -HI
unstable Co(I) hydride.
RI
RI
i) -HI
ii) +RI
I-
I-
ClO4-
ClO4-
R = CH2Si(CH3)3

Scheme 1.

N.m.r. spectrum of $[Co(CH_2Si(CH_3)_3)_2(bipy)_2]ClO_4$. ($CDCl_3$ solution.)



Spectrum 6.

would have shown the normal bipyridyl pattern consisting of two doublets for the 3,3' and 6,6' protons, and two triplets for the 4,4' and 5,5' protons. The cis-isomer was preferentially formed because steric hindrance would be smaller than in the trans-compound. The characteristic trimethylsilylmethyl peaks in the infra-red were observed :

$\delta_{sym}(CH_3)$ — 1255, 1240, 1235sh cm^{-1}

$\nu(Si-CH_3)$ — 849, 825 cm^{-1}

$\nu(Co-C)$ — 550 cm^{-1}

MANGANESE COMPLEX.

Methyl [63] and ethyl [64] pentacarbonyl manganese are well known, the latter being an unstable, air-sensitive, volatile liquid, decomposing slowly in the dark, in vacuo, and at low temperatures.

By contrast, the trimethylsilylmethyl derivative, $MnR(CO)_5$, is a yellow liquid which can be handled in air for short periods without decomposition. It was prepared from bromopentacarbonyl-manganese and trimethylsilylmethyl-lithium. The n.m.r. spectrum showed singlets at τ 9.88 and τ 10.78 for the methyl and the methylene resonances respectively of the R group. Characteristic peaks were observed in the infra-red spectrum :

$\delta_{sym}(CH_3)$ — 1257, 1246 cm^{-1}

$\nu(Si-CH_3)$ — 846, 825 cm^{-1}

$\nu(C=O)$ — 2004s, 2000s, 1978m cm^{-1}

The compound reacted with carbon monoxide to give a new peak in the i.r. at 1797 cm^{-1}, indicating that insertion had occurred to give the acyl compound. This was not however isolated.

Thus trimethylsilylmethylpentacarbonyl-manganese is much more stable than its ethyl analogue, as expected from the postulations given previously. It may be noted that the compound, $(CO)_5MnGe_2H_5$ [65], recently prepared, is said to be thermally stable. Although this could be due to increased Mn-Ge bond strength as compared to the Mn-C bond strength, the kinetic stability could, nevertheless, result from the impossibility of alkene elimination.

TITANIUM COMPLEX.

The trimethylsilylmethyl complex, $(\pi\text{-}C_5H_5)_2TiR_2$, has been prepared from the dichloro compound $(\pi\text{-}C_5H_5)_2TiCl_2$ and the lithium reagent LiR. It was isolated as stable, yellow crystals which were slightly air-sensitive. The lower dialkyls are very unstable, although the chloroalkyls, $(\pi\text{-}C_5H_5)_2TiClR$, have much higher stability [66].

The n.m.r. spectrum showed singlets at τ 9.97 and τ 9.10 respectively for the methyl and the methylene resonances of the trimethylsilylmethyl groups. The π-cyclopentadienyl protons occurred as a singlet at τ 4.11.

The characteristic peaks for trimethylsilylmethyl complexes were observed in the infra-red spectrum :

$\delta_{sym}(CH_3)$ — 1252, 1242 cm^{-1}

$\nu(Si\text{-}CH_3)$ — 835, 807 cm^{-1}

STERIC FACTORS INFLUENCING THE STABILITY OF ALKYL COMPLEXES.

The importance of β-elimination as a mechanism for the decomposition of transition metal alkyl compounds has been discussed in the previous section. It has been shown that by using alkyl ligands which are not susceptible to such an elimination, many new stable alkyl derivatives of transition metals have been prepared and isolated.

An analogous β-elimination process is responsible for the decomposition of alkyl-lithium compounds, such as n-butyl-lithium -

$$CH_3CH_2CH_2CH_2Li \longrightarrow LiH + CH_2{=}CHCH_2CH_3 \quad [67]$$

The most likely mechanism for this decomposition is through a concerted 4-centre transition state [67] -

$$RCH_2CH_2M \longrightarrow \begin{matrix} RCH & CH_2 \\ \vdots & \vdots \\ H & M \end{matrix} \longrightarrow \begin{matrix} RCH = CH_2 \\ H - M \end{matrix}$$

Such a transition state also seems likely for transition metal alkyl compounds which are known to decompose by a well-defined concerted mechanism -

$$LCuCH_2CD_2C_2H_5 \longrightarrow LCuD + CH_2{=}CDC_2H_5 \quad [25]$$

$$R_2FeCH_2CD_2CH_2CH_2Ph \xrightarrow{\Delta} R_2FeD + CH_2{=}CDCH_2CH_2Ph \quad [26]$$

The 4-membered transition state accounts for the specific transference of hydrogen or deuterium from the β-position on to the metal, but is probably an over-simplification for the true processes involved. Free radical mechanisms cannot be involved since no coupled products were formed.

However, if such a 4-membered transition state can be prevented, then β-elimination should not occur and stable compounds should ensue. It was with this intention in mind that reactions of

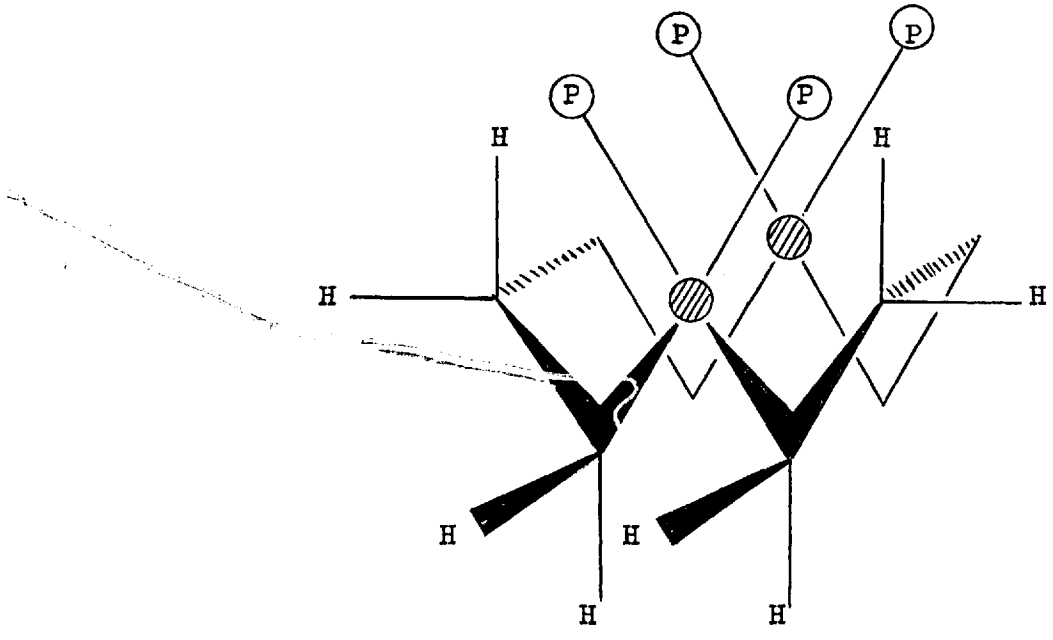
several platinum and palladium complexes were attempted with the double-ended Grignard reagents derived from 1,4-dibromobutane and 1,5-dibromopentane. Chelated compounds of the type $(PMe_2Ph)_2Pt(CH_2)_n$ where n is 4 or 5 were expected to be produced. With the alkyl groups fixed in this configuration, a 4-membered transition state could not be achieved, and the compounds should therefore be stable to β-elimination. Molecular weight determinations on the products, however, showed that the compounds were dimeric, and that the structures must consist of two metal atoms linked by two chains of methylene groups. The alkyl groups were thus still fixed in a configuration from which a 4-membered transition state could not be achieved, and the platinum derivatives were indeed found to be very stable. The palladium analogues could not however be isolated.

The dichloro platinum compound, cis-$PtCl_2(PMe_2Ph)_2$, reacted with the double-ended Grignard reagent, $BrMg(CH_2)_4MgBr$, to give the dimer $[Pt(PMe_2Ph)_2(CH_2)_4]_2$ as colourless crystals. These were extremely stable in air for many months and stable in solution for several days.

The n.m.r. spectrum showed two very broad peaks at τ 7.55 and τ 7.78 in the intensity ratio 1:1 for the four methylene groups directly bonded to platinum and the four methylene groups inbetween these, respectively. The methylene groups directly bonded to platinum had non-equivalent protons which were coupled to adjacent methylene protons and to the phosphorus atom trans to them giving a complex pattern with platinum satellites. This pattern could not be resolved however and only a broad peak was observed. The other methylene protons should also have shown a complex pattern since the protons in the CH_2 group are non-equivalent and are coupled to two different methylene groups in adjacent positions. Again, all that was observed was a broad unresolved peak. The methyls of the

dimethylphenylphosphine groups occurred as a doublet centred at τ 8.75, due to coupling with the phosphorus atom, with ^{195}Pt satellites (J(P-H) = 7.5 Hz, J(Pt-H) = 18 Hz). The doublet pattern showed that the phosphine groups were in a cis configuration [42]. The n.m.r. is shown in Spectrum 7.

Molecular models would suggest that a stable structure for $[Pt(PMe_2Ph)_2(CH_2)_4]_2$ would be as shown in Figure 4, but an X-ray analysis has not been carried out to verify this. It may be seen that the β-hydrogens are distant from any vacant sites on platinum.

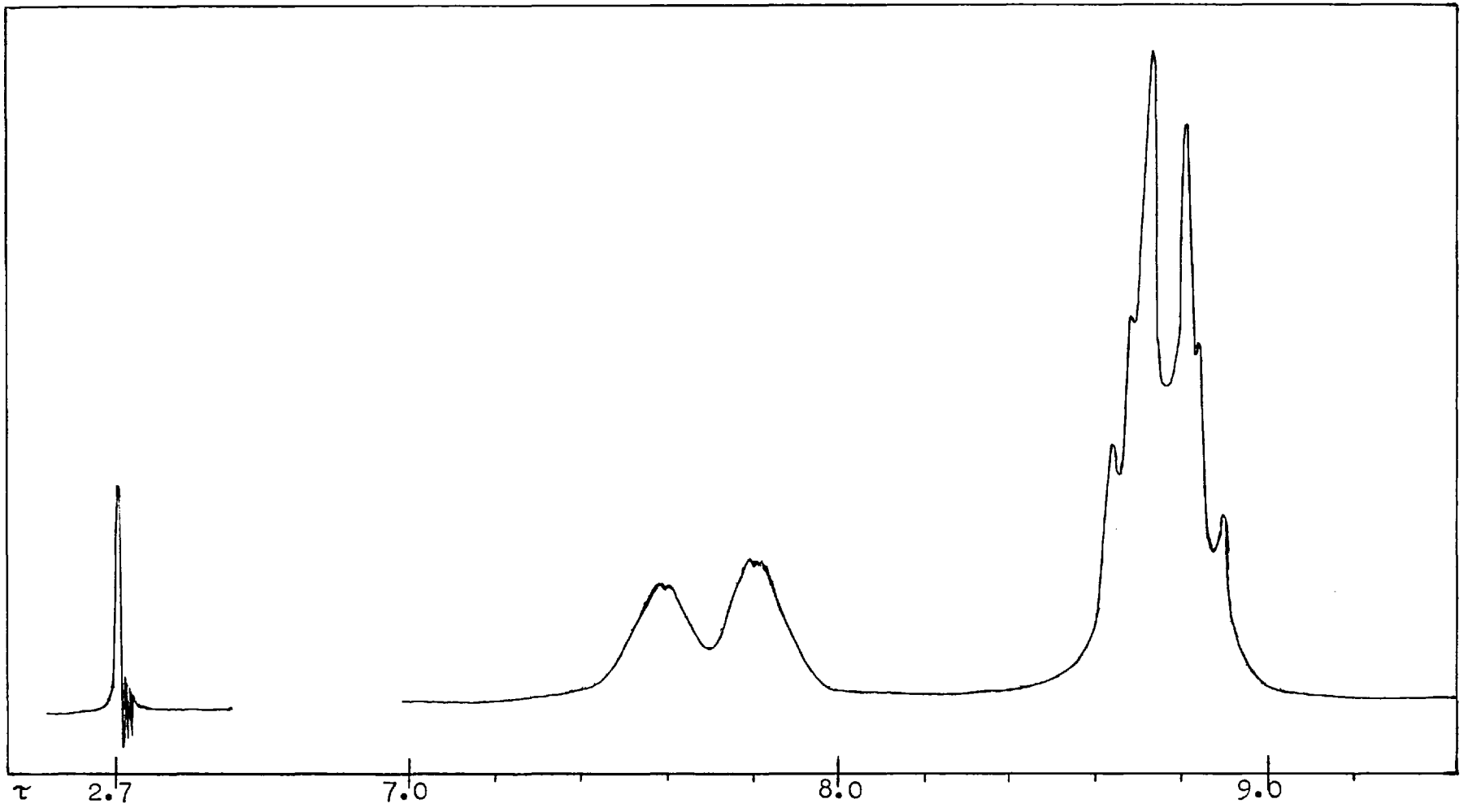


Ⓟ = (PMe_2Ph)

● = Pt

Figure 4.

N.m.r. spectrum of $\left[Pt(PMe_2Ph)_2(CH_2)_4\right]_2$. (Benzene solution.)

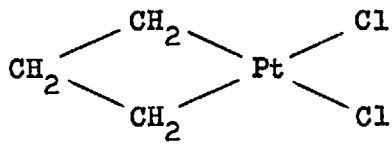


Spectrum 7.

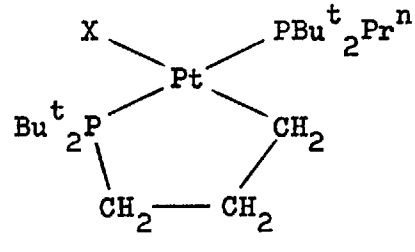
With the double-ended Grignard reagent, $BrMg(CH_2)_5MgBr$, the dichloro compound, cis-$PtCl_2(PMe_2Ph)_2$, gave colourless crystals of the dimer, $[Pt(PMe_2Ph)_2(CH_2)_5]_2$. This compound was also extremely stable both in the solid state and in solution. The n.m.r. spectrum showed two peaks for the methylene groups. One was broad and slightly pointed at τ 7.73, and the other was very broad and flat at τ 8.10. These were of intensity ratios 2:3 and were due to the four methylene groups directly bonded to platinum and the six methylene groups in between these, respectively. As with the lower homologue, none of the fine splitting of the protons was observed. The methyls of the dimethylphenylphosphine occurred as a doublet centred at τ 8.77 with platinum satellites (J(P-H) = 7.5 Hz, J(Pt-H) = 19.5 Hz)

Reactions of the double-ended Grignard reagents with the dichloropalladium compound, cis-$PdCl_2(PEt_3)_2$, gave yellow crystals which however decomposed rapidly on isolation.

Thus platinum compounds with bridging alkyl groups are shown to be very stable, probably because the 4-membered transition state involved in a β-elimination process cannot be formed due to the rigid configuration of the alkyl chains. Several chelated platinum complexes have also been isolated and are found to be quite stable. Examples of these are shown in Figure 5.



Ref. 68.



Ref. 69.

Figure 5.

These also have a rigid configuration of alkyl groups and so are stable to β-elimination.

Several examples of compounds with one bridging chain of methylenes are known, such as -

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_n$ where n is 3, 4, 5 and 6 [37],

$[(\pi\text{-}C_5H_5)Fe(CO)_2(CH_2)_mSi(CH_3)_3]$ where m is 1 and 3 [70], and

$[(CO)_5Mn]_2(CH_2)_3$ [71].

No other examples of compounds with two bridging chains of methylenes have yet been reported.

EXPERIMENTAL.

Microanalyses were by the Microanalytical Laboratory, Imperial College. N.m.r. spectra were recorded on a Perkin-Elmer R14 (100 MHz) spectrometer, i.r. spectra on Perkin-Elmer 257 and 457 instruments, and Raman spectra on a Cary model 81 spectrophotometer with a CRL 52M6 argon-krypton laser. Molecular weights were determined on a Hitachi Perkin-Elmer Model 115 instrument. Melting points were taken on a Kofler hot-stage microscope.

MATERIALS - Chloromethyltrimethylsilane and neopentyl chloride were used as received. Iodomethyltrimethylsilane was prepared by halide exchange using potassium iodide in acetone.
Solvents were dried over sodium wire and deoxygenated before use.
Operations were carried out under nitrogen.
Excess lithium and Grignard reagents in reaction mixtures were hydrolysed by the addition of ice-cold, saturated, aqueous ammonium chloride.
All organic extracts were dried over anhydrous magnesium sulphate before evaporation.
Light petroleum refers to the fraction of boiling range 40 - 60°C.
Chromatography was carried out using acid-washed alumina (Spencer Chemicals for Industry, Type H).

Trimethylsilylmethyl-lithium [72]. — A lithium dispersion (30—40% lithium in mineral oil) (8g, 50% excess) was heated under reflux with dry toluene (100ml) for 10 min and the solvent filtered off under nitrogen. This process was repeated three times with toluene and twice with diethyl ether. Diethyl ether (50ml) was added to the clean lithium powder and the mixture stirred vigorously. Chloromethyltrimethylsilane (20g, 0.16mol) in diethyl ether (20ml) was added slowly over 1½ hr and the mixture further stirred for 1 hr. The colourless solution of trimethylsilylmethyl-lithium in diethyl ether was separated from the residual solid by filtration. The solution was stored under nitrogen at -10°C. The normality with respect to total base content was determined by hydrolysis with methanol and titration with hydrochloric acid (0.1N). Treatment of the lithium reagent with 1,2-dibromoethane, followed by hydrolysis and titration gave the normality with respect to inorganic base present. The difference between the two values gave the normality with respect to the lithium reagent (1.4N, 80% yield).

Trimethylsilylmethylmagnesium chloride [73]. — Magnesium turnings (2.4g, 0.1mol) were heated up to 150°C with efficient stirring for 30 min and were then allowed to cool to room temperature under nitrogen. Diethyl ether (50ml) and a small crystal of iodine were added. Chloromethyltrimethylsilane (12.2g, 0.1mol) was dissolved in diethyl ether (25ml) and a few ml of the mixture was added to the magnesium. If no immediate reaction occurred, a few drops of 1,2-dibromoethane were added to initiate the reaction. The remainder of the chloromethyltrimethylsilane was added slowly over 2 hr. The mixture was stirred overnight. The normality of the Grignard reagent was determined by hydrolysis with methanol and titration with hydrochloric acid (0.1N). (Grignard reagent - 0.6N, 60% yield).

Neopentyl-lithium. — This was prepared by the same method as trimethylsilylmethyl-lithium. A yellowish solution of neopentyl-lithium in diethyl ether was obtained. (1.0N, 60% yield).

PLATINUM COMPLEXES.

The starting materials, cis-$PtCl_2(PMe_2Ph)_2$ [42], cis-$PtCl_2(PPh_3)_2$ [74,44], cis-$PtCl_2(AsPh_3)_2$ [74,44], $PtCl_2$(1,5-COD) [75], $PtCl_2$(2,2'-bipy) [76], cis-$PtCl_2(py)_2$ [77], trans-$PtHCl(PEt_3)_2$ [78], and $[(CH_3)_3PtI]_4$ [39] were prepared by standard literature methods.

cis-Bis(trimethylsilylmethyl)bis(dimethylphenylphosphine)platinum. — The complex cis-dichlorobis(dimethylphenylphosphine)platinum [42], (0.6g, 1mmol) was suspended in benzene (10ml) and a solution of trimethylsilylmethyl-lithium (3mmol, 50% excess) in diethyl ether was added at 0°C. The mixture was stirred for 30 min and the excess lithium reagent was hydrolysed. The organic extract was evaporated to dryness to leave a pale yellow oil. Crystallisation (light petroleum) gave the dialkyl as colourless crystals, (0.48g, 75% yield), m.p. 50 - 51°. (Found : C, 44.5; H, 6.7. $C_{24}H_{44}P_2PtSi_2$ requires C, 44.6; H, 6.9%).

Reactions of cis-bis(trimethylsilylmethyl)bis(dimethylphenylphosphine)-platinum. — 1) cis-Bis(trimethylsilylmethyl)bis(dimethylphenyl-phosphine)platinum (0.1g) was dissolved in methyl iodide (2ml) and left in the dark for 3 days. Light petroleum was added to give pale yellow crystals of diiododimethylbis(dimethylphenylphosphine)-platinum (IV) [14], m.p. 174 - 177°. (Found : C, 28.8; H, 3.9. $C_{18}H_{28}I_2P_2Pt$ requires C, 28.6; H, 3.7%).

2) cis-Bis(trimethylsilylmethyl)bis(dimethylphenylphosphine)platinum (0.1g) was dissolved in ether (2ml) and acetylbromide (0.02g, 1 equiv.)

was added slowly with stirring. Immediately white crystals of dibromobis(dimethylphenylphosphine)platinum [42] were formed, m.p. 201 - 204°.

cis-Bis(trimethylsilylmethyl)bis(triphenylphosphine)platinum. — cis-Dichlorobis(triphenylphosphine)platinum [74,44] (0.79g, 1mmol) was suspended in diethyl ether (10ml) and a solution of trimethylsilylmethyl-lithium (3mmol) in diethyl ether was added at 0°C. The mixture was stirred for 30 min and the excess lithium reagent was hydrolysed.The organic extract was evaporated to leave a colourless solid. Crystallisation (light petroleum) gave colourless crystals of the dialkyl (0.69g, 77% yield), m.p. 148 - 149°. (Found : C, 59.8; H, 6.3. $C_{44}H_{52}P_2PtSi_2$ requires C, 59.0; H, 5.9%).

cis-Bis(trimethylsilylmethyl)bis(triphenylarsine)platinum and trans-chlorotrimethylsilylmethylbis(triphenylarsine)platinum. — 1) cis-Dichlorobis(triphenylarsine)platinum [74,44] (0.88g, 1mmol) was suspended in diethyl ether (10ml) and trimethylsilylmethyl-lithium (2mmol) in diethyl ether was added at 0°C. After hydrolysis and evaporation of the organic extract, a pale brown solid was obtained. Crystallisation from diethyl ether gave colourless crystals of cis-bis(trimethylsilylmethyl)bis(triphenylarsine)platinum (0.68g, 70% yield), m.p. 138 - 139°. (Found : C,53.6; H, 5.3. $C_{44}H_{52}As_2PtSi_2$ requires C, 53.8; H, 5.3%).
Addition of light petroleum to the brown filtrate gave pale brown crystals of trans-chlorotrimethylsilylmethylbis(triphenylarsine)-platinum (0.20g, 21% yield), m.p. 152—156°. (Found : C,51.7; H, 4.5; Cl, 4.0. $C_{40}H_{41}As_2ClPtSi$ requires C, 51.6; H, 4.4; Cl, 3.8%).

2) cis-Dichlorobis(triphenylarsine)platinum [74,44] (0.44g, 0.5mmol) was suspended in benzene (10ml) and trimethylsilylmethyl-lithium

(1.5mmol) in diethyl ether was added. The mixture was heated under reflux for 20 min. Hydrolysis and evaporation of the organic layer gave a colourless solid. Crystallisation from diethyl ether gave colourless crystals of the cis-dialkyl (0.39g, 80% yield). None of the monoalkyl was produced.

Bis(trimethylsilylmethyl)-1,5-cyclo-octadieneplatinum. — Dichloro-1,5-cyclo-octadieneplatinum [75] (0.37g, 1mmol) was reacted with trimethylsilylmethyl-lithium (3mmol) in diethyl ether at 0°C for 30 min. Hydrolysis of excess lithium reagent and evaporation of the organic extract gave a pale brown oil. Vacuum sublimation of the oil at ca. 50°C gave colourless crystals of the dialkyl (0.27g, 56% yield), m.p. 58 - 60°. (Found : C, 40.3; H, 7.1. $C_{16}H_{34}PtSi_2$ requires C, 40.2; H, 7.2%).

Bis(trimethylsilylmethyl)-2,2'-bipyridylplatinum. — Dichloro-2,2'-bipyridylplatinum [76] (0.42g, 1mmol) was suspended in diethyl ether (10ml) at -78°C and trimethylsilylmethyl-lithium (3mmol) in diethyl ether was added. After 30 min, the mixture was allowed to warm to 0°C, excess lithium reagent was hydrolysed and the organic extract was evaporated to dryness to give a dark red oil. Crystallisation (light petroleum) gave dark red crystals of the dialkyl (0.33g, 64% yield), m.p. 162 - 164°(dec.). (Found : C, 41.6; H, 5.9. $C_{18}H_{30}N_2PtSi_2$ requires C, 41.1; H, 5.8%).

Dichlorobis(dimethylsulphide)platinum. [79] — Potassium tetrachloroplatinate (2g, 5mmol) was dissolved in water (40ml) and dimethyl sulphide (1ml, 12mmol) was added. The mixture was stirred for 2 hr. The pinkish precipitate was filtered, washed with ethanol and air-dried. It was then dissolved up in a small quantity of

boiling 2-methoxyethanol, filtered and allowed to cool. Yellow crystals of the dimethyl sulphide complex were formed.

Tris[bis(trimethylsilylmethyl)(dimethyl sulphide)platinum]. — Dichlorobis(dimethyl sulphide)platinum (0.39g, 1mmol) was suspended in diethyl ether at -78°C and trimethylsilylmethyl-lithium (3mmol) in diethyl ether was added. The mixture was stirred for 10 min and then allowed to warm up to 0°C. Excess lithium reagent was hydrolysed and the organic extract was evaporated to give a colourless solid and a dark oil smelling strongly of dimethyl sulphide. Crystallisation (diethyl ether) gave colourless crystals of the trimer (0.24g, 56% yield), m.p. 130 - 135°(dec.). (Found : C, 28.2; H, 6.6; S, 7.4; M, 1261. $C_{30}H_{84}Pt_3S_3Si_6$ requires C, 27.8; H, 6.5; S, 7.4%; M, 1295).

Reactions of tris[bis(trimethylsilylmethyl)(dimethyl sulphide)-platinum]. — 1) The trimer (0.05g) was dissolved in benzene and triphenylphosphine (0.03g, 3 equivalents) in benzene was added. An n.m.r. spectrum run immediately showed that cis-bis(trimethylsilylmethyl)bis(triphenylphosphine)platinum and free dimethyl sulphide were the products.

2) The trimer (0.05g) was dissolved in benzene and pyridine (0.01g, 3 equivalents) was added. An n.m.r. spectrum run immediately showed that cis-bis(trimethylsilylmethyl)dipyridinoplatinum and free dimethyl sulphide were the products.

Reaction of cis-dichlorodipyridinoplatinum with trimethylsilylmethyl-lithium. — cis-Dichlorodipyridinoplatinum [77] (0.42g, 1mmol) was suspended in diethyl ether at -78°C and trimethylsilylmethyl-lithium (3mmol) was added. After 20 min, the mixture was allowed to warm to 0°C. The colour of the solution gradually darkened to deep red.

Hydrolysis and evaporation of the organic extract gave a dark red oil which was chromatographed on alumina in light petroleum. The four fractions in increasing order of polarity were pink, orange, pale yellow and bright yellow solutions, but all fractions showed much complexity in the n.m.r. spectra and no pure product could be isolated.

trans-Hydrido(trimethylsilylmethyl)bis(triethylphosphine)platinum. — trans-Hydridochlorobis(triethylphosphine)platinum [78] (0.47g, 1mmol) was suspended in diethyl ether (10ml) at -78°C and trimethylsilylmethylmagnesium chloride (1.5mmol) was added slowly. The mixture was stirred at -78°C for 20 min and then allowed to warm to 0°C. Hydrolysis and evaporation of the organic extract gave a colourless oil. Vacuum sublimation at ca. 50°C gave the hydrido-alkyl as a colourless oil which could not be further purified.

Reaction of tetrakis(trimethylplatinum iodide) and trimethylsilylmethyl-lithium. — Tetrakis(trimethylplatinum iodide) [39] (0.73g, 0.5mmol) and trimethylsilylmethyl-lithium (1mmol) were reacted together in diethyl ether (10ml) at -78°C. On warming up to 0°C, excess lithium reagent was hydrolysed and the organic extract evaporated to give a pale brown oil, which could not be purified.

cis-Bisneopentylbis(dimethylphenylphosphine)platinum. — cis-Dichlorobis(dimethylphenylphosphine)platinum [42] (0.6g, 1mmol) was suspended in benzene (10ml) and neopentyl-lithium (3mmol) in diethyl ether was added at 0°C. After 30 min excess lithium reagent was hydrolysed and the organic extract was evaporated to give a pale brown solid. Crystallisation (light petroleum) gave creamy coloured crystals of the dialkyl, (0.44g, 72% yield), m.p. 136 - 138°. (Found : C, 51.5; H, 7.5. $C_{26}H_{44}P_2Pt$ requires C, 50.9; H, 7.2%).

PALLADIUM COMPLEXES.

The starting material cis-$PdCl_2(PEt_3)_2$ [80] was prepared by the standard literature method.

cis-Bis(trimethylsilylmethyl)bis(triethylphosphine)palladium. — cis-Dichlorobis(triethylphosphine)palladium [80] (0.41g, 1mmol) was suspended in diethyl ether (10ml) at -78°C and a drop of triethylphosphine was added. Trimethylsilylmethyl-lithium (2.5mmol) in diethyl ether was added slowly and the mixture was stirred at -78°C for 20 min, allowed to warm to 0°C and hydrolysed. Evaporation of the organic extract gave a yellow solid. Crystallisation (light petroleum) gave pale yellow crystals of the dialkyl (0.26g, 64% yield) m.p. 60 - 62°. (Found : C, 46.1; H, 9.9. $C_{20}H_{52}P_2PdSi_2$ requires C, 46.4; H, 10.1%).

trans-Trimethylsilylmethylchlorobis(triethylphosphine)palladium. — cis-Dichlorobis(triethylphosphine)palladium [80] (0.4g, 1mmol) was suspended in diethyl ether (10ml) at -78°C and a trace of triethylphosphine was added. Trimethylsilylmethylmagnesium chloride (1.5mmol) in diethyl ether was added slowly and the mixture stirred for 30 min. It was then allowed to warm to 0°C when it slowly darkened, and was hydrolysed. The organic extract was evaporated to give a brown oil. Vacuum sublimation at ca. 40°C gave the monoalkyl as a yellow, sticky solid which could not be further purified. (0.23g, 50% yield), m.p. 32 - 34°. (Found : C, 39.6; H, 8.2. $C_{16}H_{41}ClP_2PdSi$ requires C, 41.3; H, 8.9%).

cis-Bisneopentylbis(triethylphosphine)palladium. — cis-Dichlorobis(triethylphosphine)palladium [80] (0.4g, 1mmol) was suspended in diethyl ether (10ml) at -78°C and a drop of triethylphosphine was added. Neopentyl-lithium (2.5mmol) in diethyl ether

was added and the mixture stirred for 15 min. On allowing to warm to 0°C the solution rapidly darkened in colour. Hydrolysis and evaporation of the organic extract gave a brown oil. Crystallisation (light petroleum) gave yellow-brown crystals of the dialkyl which immediately turned black on isolation. An analytically pure sample could not be obtained.

Reactions of cis-bis(trimethylsilylmethyl)bis(triethylphosphine)-palladium and trans-trimethylsilylmethylchlorobis(triethylphosphine)-palladium with carbon monoxide. —

1) cis-Bis(trimethylsilylmethyl)bis(triethylphosphine)palladium (0.05g) was dissolved in light petroleum and carbon monoxide was bubbled through the solution for 30 min. The solution immediately changed colour to orange and gradually darkened to orange-red. Evaporation of the solvent gave a red oil which immediately turned black in air. The i.r. (cyclohexane) showed ν(CO) terminal - 2000m, 1960s, and 1940w cm^{-1} and ν(CO) bridging - 1830s and 1805s cm^{-1}. The product was not isolated pure.

2) trans-Trimethylsilylmethylchlorobis(triethylphosphine)palladium (0.05g) was dissolved in light petroleum and carbon monoxide was bubbled through the solution for 30 min. The yellow solution was evaporated to dryness to give a yellow oily product. I.r. (cyclohexane) showed ν(acyl) at 1640 cm^{-1} but the product was not isolated pure.

GOLD COMPLEXES.

The starting materials $ClAuPPh_3$ [58] and $HAuBr_4$ [58] were prepared by the standard literature methods.

Trimethylsilylmethyltriphenylphosphinegold. —

1) Chlorotriphenylphosphinegold [58] (0.49g, 1mmol) was suspended in diethyl ether (10ml) at -78°C and trimethylsilylmethyl-lithium (1.5mmol)

in diethyl ether was added slowly. The mixture was stirred at -78°C for 20 min, allowed to warm to 0°C and hydrolysed. Evaporation of the organic extract gave a white solid. Crystallisation (diethyl ether) gave white crystals of the alkyl, (0.41g, 75% yield), m.p. 111 - 113°. (Found : C, 48.0; H, 4.6; M, 572. $C_{22}H_{26}AuPSi$ requires C, 48.3; H, 4.8% ; M, 546).

2) Bromoauric acid [58] (0.51g, 1mmol) was dissolved in diethyl ether (10ml) at -78°C. Trimethylsilylmethylmagnesium chloride (3mmol) and triphenylphosphine (1mmol) in diethyl ether were added slowly. The mixture was stirred at -78°C for 20 min, allowed to warm to 0°C and hydrolysed. The organic extract was evaporated to give a white solid. Crystallisation (diethyl ether) gave white crystals of the alkyl, (0.32g, 60% yield), m.p. 111 - 113°.

A mixture of the products from method 1) and 2) gave a m.p. 111 - 113°, indicating that the same alkyl, trimethylsilylmethyltriphenylphosphine-gold, was produced in each case.

Neopentyltriphenylphosphinegold. — Chlorotriphenylphosphinegold [58] (0.49g, 1mmol) was suspended in diethyl ether (10ml) at -78°C and neopentyl-lithium (1.5mmol) was added slowly. After 20 min the solution was allowed to warm up to 0°C, hydrolysed and the organic extract evaporated to give a pale brown oil. Crystallisation (diethyl ether) gave pale brown crystals of the alkyl, which could not be further purified, (0.37g, 70% yield) m.p. 114 - 117°. (Found : C, 54.3; H, 5.4. $C_{23}H_{26}AuP$ requires C, 52.1; H, 4.9%).

Methyldiphenylphosphinetrimethylsilylmethylgold. — Bromoauric acid [58] (o.51g, 1mmol) was dissolved in diethyl ether (10ml) at -78°C. Trimethylsilylmethylmagnesium chloride (3mmol) and methyldiphenyl-phosphine (1mmol) in diethyl ether were added slowly. The mixture was stirred at -78°C for 20 min, allowed to warm to 0°C and hydrolysed.

The organic extract was evaporated to give a white oily product. Crystallisation (light petroleum) gave white crystals of the alkyl, (0.29g, 60% yield), m.p. 65 -70°. (Found : C, 42.90; H, 5.04. $C_{17}H_{24}AuPSi$ requires C,42.15; H, 4.96%).

Reaction of bromoauric acid with trimethylsilylmethylmagnesium chloride. — Bromoauric acid [58] (0.51g, 1mmol) was dissolved in diethyl ether (10ml) at -78°C and trimethylsilylmethylmagnesium chloride (2.5mmol) was added. Light was excluded from the apparatus. After 30 min the mixture was allowed to warm to 0°C and was hydrolysed. The organic extract was evaporated and a brownish solid was obtained. This decomposed readily on exposure to air and light, and could not be purified further.

COBALT COMPLEX.

Bis(trimethylsilylmethyl)bis-2,2'-bipyridylcobalt (III) perchlorate. — Cobalt chloride (0.48g, 2mmol) was dissolved in methanol (20ml) and 2,2'-bipyridyl (0.64g, 4mmol) in methanol (20ml) was added. Iodomethyltrimethylsilane (2ml) was added and small amounts of sodium borohydride (in excess, ca. 6mmol) were added slowly until the mixture had turned red. Sodium perchlorate (2mmol) in water (20ml) was added to it and the mixture was filtered and evaporated to remove methanol. The red solid produced was recrystallised from methanol-water to give orange-red crystals of the dialkyl, (0.65g, 50% yield), m.p. 155 - 156°(dec.). (Found : C, 51.6; H, 5.8; N, 8.5; Cl, 5.3. $C_{28}H_{38}N_4ClCoO_4Si_2$ requires C, 52.1; H, 5.9; N, 8.7; Cl, 5.5%).

MANGANESE COMPLEX.

The starting material $Mn(CO)_5Br$ [81], was prepared by the standard literature method.

Trimethylsilylmethylpentacarbonylmanganese *. —
Bromopentacarbonylmanganese [81] (1.3g, 5mmol) in diethyl ether (150ml) was cooled to -78°C and trimethylsilylmethyl-lithium (5.25mmol) in diethyl ether was added. On warming to room temperature the solution turned dark red. Diethyl ether was removed and the solid residue extracted with light petroleum (b.p. 30 - 40°C) to give a red solution. Evaporation of the solvent gave a brown oil which was distilled at 22°C under high vacuum to give the alkyl as a yellow liquid, (0.70g, 50% yield) m.p. -5°. (Found : C, 39.3; H, 3.9. $C_9H_{11}MnO_5Si$ requires C, 38.2; H, 3.9%).

* This compound was prepared by Tony Shortland.

TITANIUM COMPLEX.

The starting material $(\pi\text{-}C_5H_5)_2TiCl_2$ [82], was prepared by the standard literature method.

Bis(trimethylsilylmethyl)di(π-cyclopentadienyl)titanium *. —
Dichlorodi(π-cyclopentadienyl)titanium [82] (2.5g, 10mmol) in diethyl ether was cooled to -78°C and trimethylsilylmethyl-lithium (22mmol) in diethyl ether was added. The mixture was allowed to warm to room temperature, filtered and the ether removed. The residue was extracted into light petroleum, filtered and the brown solution evaporated. Vacuum sublimation at 60 - 80°C from the residue gave yellow crystals of the dialkyl. This can be purified by chromatography on alumina with light petroleum, (1.4g, 40% yield), m.p. 185°C. (Found : C, 59.7; H, 8.5. $C_{18}H_{21}Si_2Ti$ requires C, 61.3; H, 9.1%).

* This compound was prepared by Walter Mowat.

COMPLEXES WITH BRIDGING ALKYL GROUPS.

1,4-Bis(bromomagnesium)butane. — Magnesium turnings (9.6g, 0.4mol) were covered with diethyl ether (400ml) and a crystal of iodine was

added. 1,4-Dibromobutane (43g, 0.2mol) was added slowly over ½ hr and the mixture heated under reflux for 3 hr. A colourless solution of the double-ended Grignard reagent in diethyl ether was obtained, (0.4M, 80% yield).

1,5-Bis(bromomagnesium)pentane. — This was similarly prepared from 1,5-dibromopentane to give a colourless solution of the Grignard reagent in diethyl ether, (0.35M, 70% yield).

Bis[tetramethylenebis(dimethylphenylphosphine)platinum] (Figure 4) — cis-Dichlorobis(dimethylphenylphosphine)platinum [42] (0.6g, 1mmol) was suspended in benzene (10ml) and the double-ended Grignard reagent, $BrMg(CH_2)_4MgBr$, (2mmol) in diethyl ether was added. The mixture was stirred for 2 hr, hydrolysed and the organic extract evaporated to give a colourless solid. This was recrystallised (light petroleum) to give colourless crystals of the dimer, (0.42g, 80% yield), m.p. 127 - 131°C. (Found : C, 45.7; H, 5.8; M, 1056. $C_{40}H_{60}P_4Pt_2$ requires C, 45.5; H, 5.7%; M, 1055).

Bis[pentamethylenebis(dimethylphenylphosphine)platinum]. — This was similarly prepared from cis-dichlorobis(dimethylphenylphosphine)platinum [42] and $BrMg(CH_2)_5MgBr$. Colourless crystals of the dimer were obtained from light petroleum, (0.38g, 70% yield), m.p. 111 - 114°. (Found : C, 46.5; H, 5.9; M, 1187. $C_{42}H_{64}P_4Pt_2$ requires C, 46.6; H, 5.9%; M, 1083).

Reactions of cis-dichlorobis(triethylphosphine)palladium with 1,4-bis(bromomagnesium)butane and 1,5-bis(bromomagnesium)pentane. — cis-Dichlorobis(triethylphosphine)palladium [80] (0.4g, 1mmol) was dissolved in diethyl ether (10ml) at -78°C and a trace of triethyl-

phosphine was added. 1,4-Bis(bromomagnesium)butane (2.5mmol) was added and the mixture stirred for 10 min and allowed to warm to room temperature, when it began to darken. Hydrolysis and evaporation of the organic extract gave a red oil. Crystallisation from light petroleum gave orange crystals which immediately blackened on isolation. No pure product could be isolated.

Exactly the same reactions were observed with 1,5-bis(bromomagnesium)-pentane, and no pure product could be isolated.

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COMPLEX CHEMISTRY OF RUTHENIUM WITH THE CARBOXYLATO FUNCTION.

INTRODUCTION.

The first study of ruthenium carboxylate compounds was by Mond [1] who obtained a series of complexes formulated as binuclear species, by refluxing a hydrated ruthenium (III, IV) oxide with the carboxylic acid. The reproducibility of these reactions was questioned and seemed to depend on the water content of the ruthenium oxide starting material [2]. However the main product with acetic acid was found to be a trinuclear oxo-acetate [3], $[Ru_3O(OAc)_6(OAc)_3]^{(2-)}$, which has an analogous structure to the basic acetates of chromium (III) and iron (III). The latter two complexes and the basic manganese (III) acetate have been shown by X-ray crystallography to contain the trinuclear oxygen-centred cation, $[M_3O(OAc)_6(H_2O)_3]^{(+)}$, (M = Cr [4,5], Mn [6] or Fe [4,7]). Recently, analogous acetates of cobalt [8] and rhodium [9] have also been prepared.

By reduction, with acetaldehyde, of solutions of ruthenium tetroxide in acetic acid - carbon tetrachloride mixtures, Martin [10] obtained a complex also thought to be analogous with the chromium and iron acetates, viz. $[Ru_3O(OAc)_6](OAc).8H_2O$, and the Raman spectrum for the compound was interpreted accordingly [11]. However it has been shown that Martin's acetate is not oxygen-centred and is probably polymeric, containing mainly ruthenium (III) [3], but its exact nature is still not known.

By the interaction of commercial ruthenium trichloride with acetic acid - acetic anhydride mixtures, the tetra-acetato-bridged binuclear complex, $[Ru_2(OAc)_4]Cl$, was obtained [2] (Figure 1). An X-ray crystallographic study of this compound [12] showed that the $[Ru_2(OAc)_4]^{(+)}$ units were linked into chains by Ru - Cl - Ru bridges. The interaction of ruthenium trichloride, acetic acid, and sodium acetate in ethanol gave an impure green material believed to be the

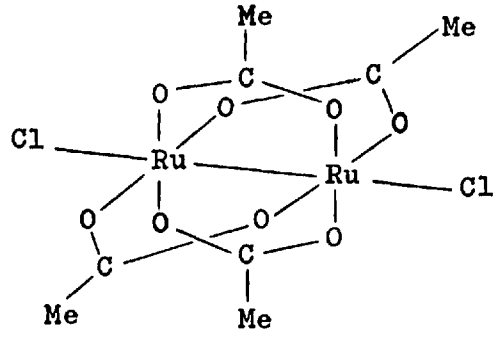


Figure 1.

corresponding neutral dimer, $Ru_2(OAc)_4$ [13]. This was shown to form adducts with pyridine and triphenylphosphine which were believed to be analogous to the well-known adducts of the dimeric tetra-bridged acetates of chromium (II), copper (II) and rhodium (II) [12].

However, electrochemical studies and molecular weight determinations indicated that the green acetate was not $Ru_2(OAc)_4$, but rather a ruthenium (III) complex of the basic acetate, trinuclear oxygen-centred type [3]. An X-ray crystallographic study of the triphenylphosphine derivative [14] proved that this was the structure and that the complex was $Ru_3O(OAc)_6(PPh_3)_3$ (Figure 2). Careful purification and analysis of the parent green acetate showed it to have the stoicheiometry $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ [3,14], and that it was also analogous to the basic chromium and iron acetates.

The acetate was paramagnetic with μ_{eff} = 1.77 B.M.[3], a value consistent with a $Ru(III)_3O$ unit, in which marked spin-spin interaction would be expected <u>via</u> the central oxygen atom. This type of magnetic interaction was first postulated for the basic chromium acetate complex [15,16], where the chromium-chromium distance [4,5] was too large for magnetic exchange to arise from a direct metal-metal interaction. The trinuclear oxygen-centred acetates are thus intermediate in character [16] between magnetically dilute systems,

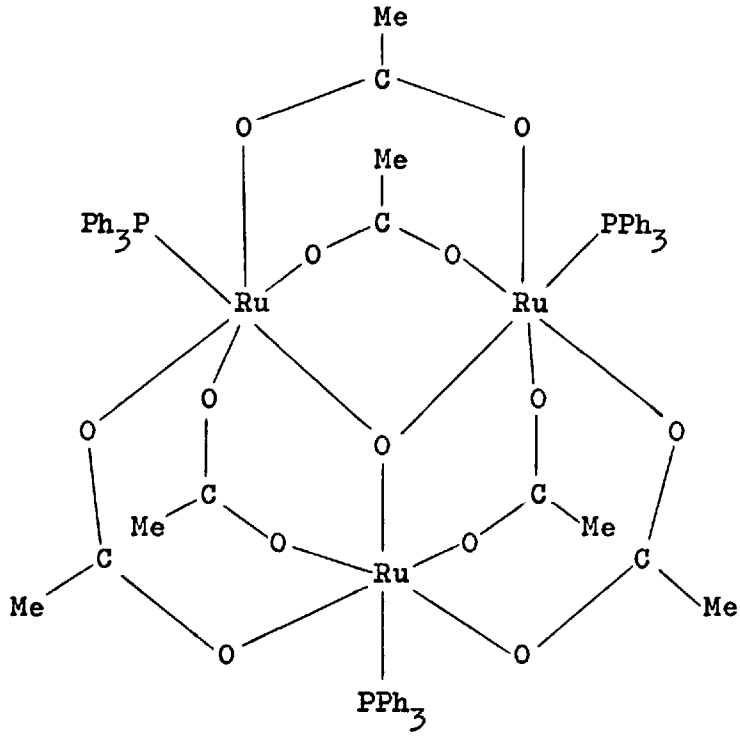
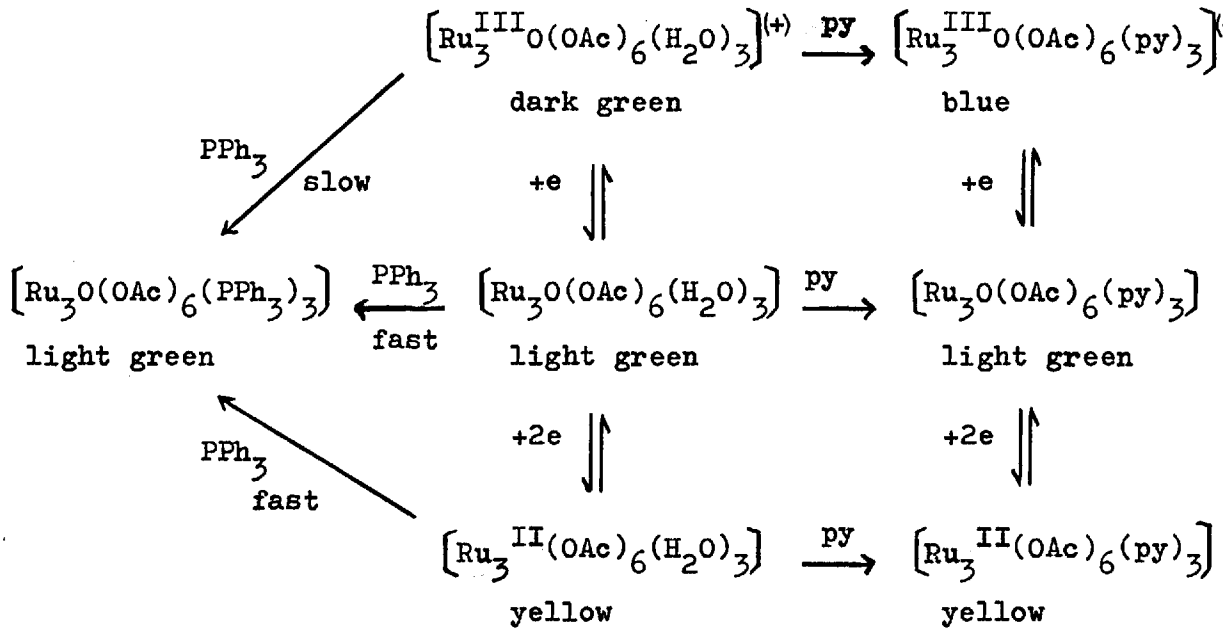


Figure 2.

where normal paramagnetism occurs, due to negligible magnetic interactions between the magnetic ion and other ions, and magnetically concentrated systems, where the magnetic ion interacts with other ions and ferro- and antiferro-magnetism arises.

The acetate $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ underwent reversible reductions in methanol at room temperature with hydrogen at 2 atmospheres pressure over a platinum oxide catalyst. The blue pyridine complex, $[Ru_3O(OAc)_6(py)_3]^{(+)}$, was similarly but more rapidly reduced. The triphenylphosphine complex, $Ru_3O(OAc)_6(PPh_3)_3$, was not reduced at room temperature. These reactions [3] are summarised in Scheme 1, and are common to other carboxylic acid derivatives.

Electrochemical studies [3] proved that the first stage was a one electron reduction and the second stage a further two electron reduction. The reversibility of the reductions showed that the



Scheme 1.

trinuclear structure was always retained. The light green species, counterparts of the diamagnetic species $Ru_3O(OAc)_6(PPh_3)_3$, had the ruthenium atoms in a mean oxidation state $2\frac{2}{3}$, *i.e.* Ru(II, III, III). The fully reduced yellow species were formed by a two electron reduction, requiring removal of the central oxygen atom, to give a trinuclear carboxylato-bridged complex containing formally three, five-coordinate ruthenium (II) atoms. The yellow complexes were extremely sensitive to oxygen. A single oxygen atom could be re-inserted into the yellow complexes by using the stoicheiometric amount of pyridine-N-oxide under rigorously oxygen-free conditions. G.l.c. analysis confirmed that pyridine was produced in the expected amounts [3]:

$$[Ru_3(OAc)_6(Mepy)_3] + C_5H_5NO \longrightarrow [Ru_3O(OAc)_6(Mepy)_3] + C_5H_5N$$

The yellow complexes were weakly paramagnetic with μ_{eff} *ca.* 0.4 B.M. *per* Ru_3 unit.

The triphenylphosphine complexes of the acetate, propionate, and n-butyrate (mean oxidation state $2\frac{2}{3}$) also underwent a two

electron reduction, but this was irreversible, leading to a break-up of the trinuclear cluster [3]. The acetate complex gave the yellow compound, $Ru(OAc)_2PPh_3.nMeOH$ [17]. Solutions of this compound were oxidised by air to a new type of oxo-bridged ruthenium (III) complex, $Ru_2O(OAc)_4(PPh_3)_2$. This did not show any bands in the region of the i.r. characteristic for linear M-O-M bonds, and it is proposed that the Ru-O-Ru group is bent [17], giving a structure as shown in Figure 3 :

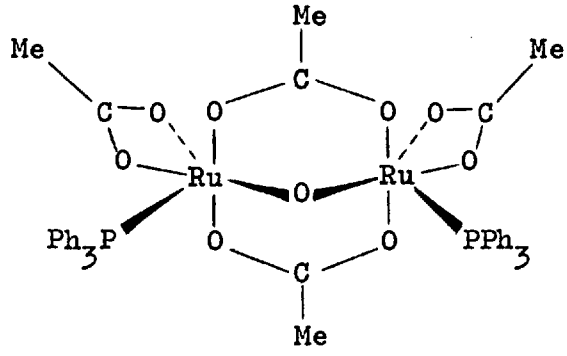


Figure 3.

This purple compound was diamagnetic [17], spin-spin interaction occurring through the bent Ru(III)-O-Ru(III) bridge in a similar manner to that discussed previously.

The trinuclear oxo-centred triphenylphosphine compound, $Ru_3O(OAc)_6(PPh_3)_3$, when protonated with fluoroboric acid and excess triphenylphosphine added, was active as a catalyst for the hydrogenation of alkenes [13]. The binuclear oxo-bridged compound, $Ru_2O(OAc)_4(PPh_3)_2$, was also catalytically active under similar conditions [17].

RESULTS AND DISCUSSION.

The acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, has now been well characterised as being of the basic acetate, oxygen-centred, trinuclear type [3,14], and its pyridine and triphenylphosphine derivatives have analogous structures. Several reactions were carried out with these compounds to see if the oxo-triruthenium cluster was preserved or broken up to form mononuclear complexes.

Reactions with simple ligands such as carbon monoxide, nitric oxide, sulphur dioxide and triphenylphosphite appeared to retain the cluster, but with sodium diethyl and dimethyl dithiocarbamate, 2-mercaptobenzthiazole and diphenyldithiophosphoric acid, there was a tendency for the trinuclear strucure to break up.

COMPLEXES WITH CARBON MONOXIDE.

The light green reduced acetate, $Ru_3O(OAc)_6(H_2O)_3$, (Scheme 1), reacted almost instantaneously with carbon monoxide at 2 atmospheres pressure, in methanol, to give a purple solution, from which the carbonyl compound, $Ru_3O(OAc)_6(CO)(CH_3OH)_2$, was isolated by chromatography on Sephadex (grade G10). The complex was obtained as purple crystals from methanol. The same compound was also obtained with the yellow, fully reduced Ru(II) species, $Ru_3(OAc)_6(H_2O)_3$, and with the dark green Ru(III) species, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, although the latter was very slow in reacting, requiring over 24 hr before complete reaction occurred. The purple complex, $Ru_3O(OAc)_6(CO)(CH_3OH)_2$, was soluble in water, alcohols and acetone, but not in any non-polar organic solvents. The molecular weight determination, (methanol, water), indicated a trinuclear structure. The infra-red spectrum showed the carbonyl stretching frequency at 1960 cm^{-1}.

The ^1H n.m.r. spectrum in CD_3OD showed two sharp peaks for the acetate protons at τ 7.99 and τ 8.13 in the ratio 2:1 respectively. This was to be expected from the structure of the complex which had four acetate groups adjacent to the carbonyl group and to one coordinated CH_3OH molecule, and two acetate groups adjacent to two CH_3OH molecules, and hence in a different environment (Figure 4).

High voltage paper electrophoresis at pH values of 1.8, 7.0, and 9.2 showed that the carbonyl complex was a neutral species, no migration of the spot being observed at these pH values. This suggested that no coordinated water molecules were present, confirming the formula $Ru_3O(OAc)_6(CO)(CH_3OH)_2$.

The compound was found to be paramagnetic with μ_{eff} = 2.93 B.M. at 293°K in the solid state (Evans' refinement of the Gouy-Rankine Balance).

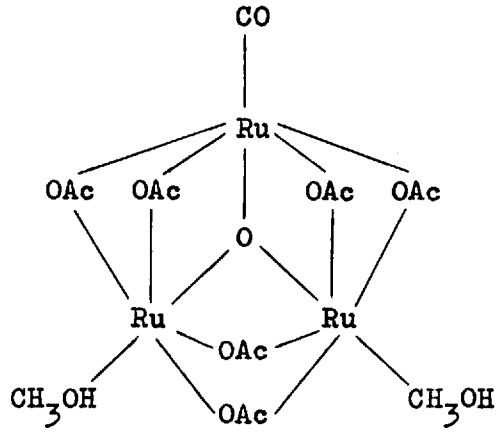


Figure 4.

This was very close to the spin-only value for two unpaired electrons, μ_{eff} = 2.83 B.M. This was the expected value for the complex, containing Ru(III, III, II), and in this case, no spin-pairing *via* the central oxygen atom had occurred. The trinuclear oxygen-centred ruthenium complexes possess a range of magnetic moments. The aquo-acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, has μ_{eff} = 1.77 B.M. [3] and the pyridine derivative, $[Ru_3O(OAc)_6(py)_3](ClO_4)$, has μ_{eff} = 2.46 B.M. [3]. Both these complexes contain three Ru(III) atoms, and would both have an expected μ_{eff} = 3.87 B.M. Thus spin-pairing *via* the central oxygen atom occurs to different degrees in these compounds, depending on the ligand fields of the surrounding groups. However, the magnetic behaviour of the compounds is not well understood at present, and will not be dealt with to any great depth.

The polarogram of the carbonyl compound in acetone, using sodium perchlorate as base electrolyte, showed two cathodic waves of similar heights at $E_{\frac{1}{2}}$ = -0.91V and $E_{\frac{1}{2}}$ = -1.40V (*v.* S.C.E.). The value of the $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ separation for the first wave at -0.91V was consistent with a reversible one-electron reduction. This was confirmed by the *n*-value of 1.2 given by a controlled potential electrolysis at -1.0V. The second wave at -1.40 V was irreversible,

but a comparison of wave heights indicated that this also was a one electron reduction. Thus the following reductions are proposed —

$$\text{Ru(III, III, II)} \xrightarrow[-0.91V]{e} \text{Ru(III, II, II)} \xrightarrow[-1.40V]{e} \text{Ru(II, II, II)}$$

For the compounds previously studied [3], the reduction from Ru(III, III, II) to Ru(II, II, II) had always proceeded by a two-electron step, but the carbonyl compound, $Ru_3O(OAc)_6(CO)(CH_3OH)_2$, was novel in that two, separate, one-electron steps were observed.

The purple carbonyl compound, $Ru_3O(OAc)_6(CO)(CH_3OH)_2$, reacted readily with pyridine to give deep blue crystals of the complex, $Ru_3O(OAc)_6(CO)(py)_2$. The same compound was formed in low yields by bubbling carbon monoxide for several hours through a methanolic solution of the pyridine complex, $[Ru_3O(OAc)_6(py)_3]Cl$, heated under reflux. It was also formed in low yields from the pyridine complex reacting with carbon monoxide at two atmospheres pressure at room temperature. The compound, $Ru_3O(OAc)_6(CO)(py)_2$, was insoluble in water and only slightly soluble in methanol, chloroform and benzene. A molecular weight determination in chloroform confirmed the trinuclear structure. The carbonyl stretching frequency occurred at 1940 cm^{-1}.

The compound was found to be slightly paramagnetic with μ_{eff} = 1.14 B.M. Thus in this Ru(III, III, II) system, partial spin-pairing <u>via</u> the central oxygen atom had occurred.

The n.m.r. spectrum ($CDCl_3$) showed two acetate peaks at τ 8.33 and τ 9.48, of intensity ratios 2:1 respectively. These were due to the four acetate groups adjacent to the carbonyl and the two acetate groups adjacent to the two pyridine groups. The pyridine resonances occurred at the very high values of τ 7.61 and τ 8.65, intensity ratios 2:3 respectively. The four peaks were all very broad, and this and the high field shifts of the pyridine protons were probably due

to the paramagnetism of the compound.

The polarogram of $Ru_3O(OAc)_6(CO)(py)_2$ in acetone showed two cathodic waves at $E_{\frac{1}{2}}$ = -1.02 V and $E_{\frac{1}{2}}$ = -1.34 V. The value of the $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ separation for the wave at -1.02 V was consistent with a reversible one-electron reduction. This was confirmed by the n-value of 0.9 given by a controlled potential electrolysis at -1.1 V. The second wave at -1.34 V was of the same height and also indicated a reversible one-electron reduction. Thus the reduction from Ru(III, III, II) to Ru(II, II, II) occurred in two one-electron steps analogous to the reduction of $Ru_3O(OAc)_6(CO)(CH_3OH)_2$. The Ru(III, II, II) species was brown and the fully reduced Ru(II, II, II) species was red. The solutions rapidly reverted to the dark blue colour of the original complex, $Ru_3O(OAc)_6(CO)(py)_2$, on exposure to air. The polarogram is shown in Figure 5.

The purple carbonyl complex, $Ru_3O(OAc)_6(CO)(CH_3OH)_2$, reacted with triphenylphosphine over several hours to give a turquoise solid, insoluble in water and methanol, and slightly soluble in chloroform. This solid was slightly air-sensitive and in solution, quickly turned dark green on exposure to air. A carbonyl stretching frequency was observed at 1945 cm^{-1}. The stoicheiometry of the compound was $Ru_2(OAc)_4(CO)(PPh_3)$ and a structure analogous to that of $[Ru_2(OAc)_4]Cl$ (Figure 1) [2,12] and $[Ru(OAc)_2(PPh_3)]_2$ [17] is proposed, with four bridging acetate groups between the two ruthenium atoms and one carbonyl and one phosphine end group.

The molecular weight of the complex in chloroform was quite low compared to the calculated value, and suggested that dissociation probably occurred in solution —

$$Ru_2(OAc)_4(CO)(PPh_3) \rightleftharpoons Ru_2(OAc)_4(CO) + PPh_3$$

The n.m.r. spectrum ($CDCl_3$) showed a single acetate peak at τ 10.06

Polarogram of $Ru_3O(OAc)_6(CO)(py)_2$. (Acetone solution.)

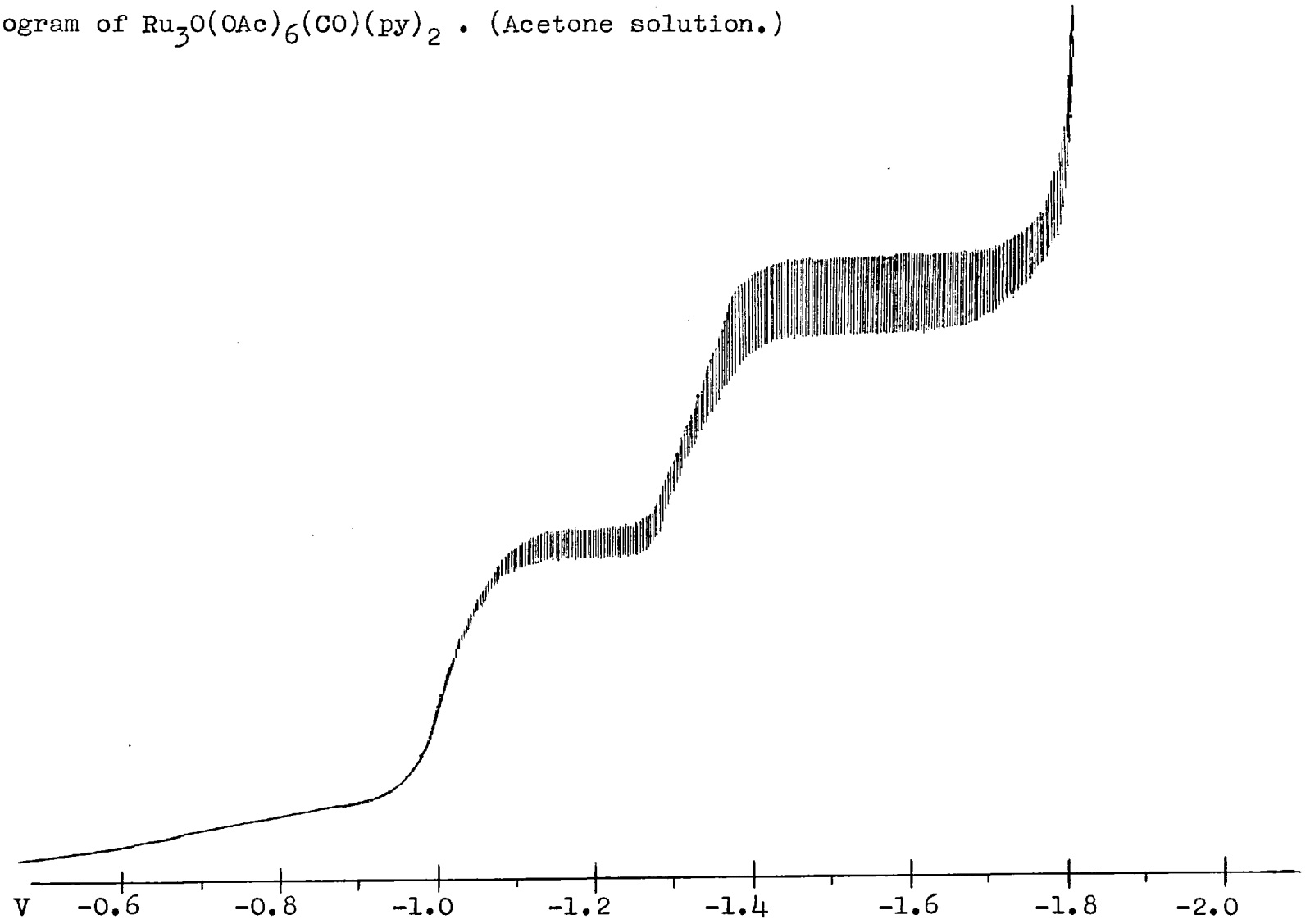


Figure 5.

and showed the presence of uncoordinated triphenylphosphine, supporting the idea of dissociation. Analogous dissociations for acetates of ruthenium are well known, e.g. —

$$Ru_2(CO)_4(OAc)_2(PPh_3)_2 \rightleftharpoons Ru_2(CO)_4(OAc)_2(PPh_3) + PPh_3$$ [18]

The compound was slightly paramagnetic, with μ_{eff} = 1.21 B.M. per Ru_2 unit. This was perhaps due to orbital contribution or to some temperature independent paramagnetism, but this was not investigated.

The polarogram in THF showed two oxidation waves at $E_{\frac{1}{2}}$ = +0.67V and $E_{\frac{1}{2}}$ = ca. +0.02 V (v. S.C.E.). The wave at +0.02 V was obscured by a maximum of the first kind, which was not suppressed by addition of a surfactant (Triton X-100). The wave heights however were approximately equal. Thus Ru(II, II) was probably oxidised to Ru(III, III) in two one-electron steps. The polarogram in dimethylformamide, using a rotating platinum electrode, showed only one oxidation wave at $E_{\frac{1}{2}}$ = +0.60 V. The oxidation of Ru(II, II) to Ru(III, III) thus probably took place in a single two-electron step in dimethylformamide.

On the reaction of commercial ruthenium trichloride in ethanol with carbon monoxide at two atmospheres pressure, a yellow solution was given. This contained some species, $Ru(CO)_nCl_m$ [19], which was isolated as a crude solid. This was heated under reflux in ethanol with sodium acetate and glacial acetic acid, following the standard method [3] for preparation of the trinuclear oxy-carboxylates, to see if analogues containing carbonyl groups were produced. An orange-yellow solid, insoluble in all common solvents, was produced and was shown to be the polymeric compound, $[Ru(CO)_2(OAc)]_n$ [18]. The carbonyl stretches in the infra-red spectrum agreed very closely with those given in the literature. The polymer had previously been prepared from the reaction of $Ru_3(CO)_{12}$ with acetic acid [18].

The compound, $[Ru(CO)_2(OAc)]_n$ was further characterised by its reaction with triphenylphosphine in boiling chloroform, giving yellow crystals of the dimer, $Ru_2(CO)_4(OAc)_2(PPh_3)_2$ [18]. This was fully identified by microanalysis and by comparison of the carbonyl stretching frequencies and the chemical shifts with the values given in the literature [18].

COMPLEX WITH NITRIC OXIDE.

The light green reduced acetate, $Ru_3O(OAc)_6(H_2O)_3$, reacted almost immediately with nitric oxide in methanol to give a brown solution, from which crystals of the complex, $Ru_3O(OAc)_6(NO)_2(OH)$, were isolated. The same brown complex was also readily given by the action of nitric oxide on the Ru(III) complex, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, and on the Ru(II) complex, $Ru_3(OAc)_6(H_2O)_3$. The nitrosyl complex was soluble in methanol, acetone, benzene and chloroform, but was insoluble in water. A molecular weight determination in chloroform indicated a trinuclear structure. The nitrosyl stretching frequency occurred as a broad band at 1870 cm^{-1}.

The n.m.r. spectrum ($CDCl_3$) showed two very broad lines at *ca.* τ 8.0 and τ 9.0 in the approximate ratio 2:1. These were due to the four acetate groups adjacent to the hydroxyl group and the two acetate groups adjacent to the two nitrosyl groups. The hydroxyl proton occurred at τ 6.48.

The polarogram in acetone showed a very irreversible reduction wave with an approximate $E_{\frac{1}{2}} = -0.6$ V. No determination of the number of electrons involved in the reduction could be made.

There are many known ruthenium-nitrosyl complexes, and these all have the metal formally in a divalent state and the nitric oxide bonded as NO^+ [20]. The Ru-NO grouping, charge +3, is known to be a very stable entity. If the two nitric oxide molecules in the complex $Ru_3O(OAc)_6(NO)_2(OH)$ are assumed to bond in this way, *i.e.* as NO^+, then the ruthenium atoms exist in the oxidation states Ru(III, II, II), mean oxidation state $2\frac{1}{3}$. Such an oxidation state has not previously been isolated in any analogous ruthenium acetate complexes, but it is known to exist as an intermediate in the polarographic reductions of $Ru_3O(OAc)_6(CO)(CH_3OH)_2$ and $Ru_3O(OAc)_6(CO)(py)_2$, as described

earlier. An alternative formulation with one nitric oxide molecule bonded as NO^+ and one as neutral NO, with oxidation states Ru(III, III, II), was also possible, although only one N — O stretching frequency was observed in the infra-red spectrum, in a chloroform solution. A formulation with two NO^+ ions, Ru(II, II, II) and a coordinated water molecule instead of a hydroxyl group may be discounted since the very broad lines in the n.m.r. spectrum strongly suggested that the complex was paramagnetic.

A magnetic moment determination showed that this was so, with μ_{eff} = 1.17 B.M. Thus if the complex is assumed to contain Ru(III, II, II) and two NO^+ ions, then the magnetic moment showed that spin-spin interaction <u>via</u> the central oxygen atom occurred only to a very slight extent in the complex. The over-all paramagnetism was probably responsible for the broadening of the lines in the n.m.r. spectrum.

COMPLEXES WITH SULPHUR DIOXIDE.

The light green reduced acetate, $Ru_3O(OAc)_6(H_2O)_3$, reacted with sulphur dioxide in methanol to give a deep blue solution. This was separated by chromatography on Sephadex to give the dark blue complex, $Ru_3O(OAc)_6(SO_2)(CH_3OH)_2$, and the dark blue-green complex, $[Ru_3O(OAc)_6(CH_3OH)(H_2O)_2]_2(SO_4)$.

The complex $Ru_3O(OAc)_6(SO_2)(CH_3OH)_2$ showed two broad acetate peaks in the n.m.r. spectrum (CD_3OD) at τ 8.17 and τ 8.47 in the approximate ratio 2:1. This resulted from the four acetate groups adjacent to the SO_2 group and the other two acetate groups, respectively. High voltage paper electrophoresis showed the complex was neutral at the pH values 1.8, 7.0, and 9.2. The polarogram in methanol showed one irreversible reduction wave at $E_{\frac{1}{2}}$ = -0.19 V. This was probably a two-electron reduction process, by analogy with other complexes of this type [3], Ru(III, III, II) being reduced to Ru(II, II, II).

The complex $[Ru_3O(OAc)_6(CH_3OH)(H_2O)_2]_2(SO_4)$ showed a single broad peak in the n.m.r. spectrum (CD_3OD) at τ 9.00, for the acetate protons. The high chemical shift was probably due to the paramagnetism of the complex. High voltage paper electrophoresis showed the complex migrating as a cation in an acidic (pH 1.8) medium and as an anion in a basic (pH 9.2) medium. In a neutral medium the complex existed as both cationic and neutral species. In the basic medium therefore, both water molecules in each Ru_3O unit were deprotonated, giving an anion. In the neutral medium only one of the water molecules was deprotonated. The following processes were thus occurring —

$$[Ru_3O(OAc)_6(CH_3OH)(H_2O)_2]^+ \overset{-H^+}{\rightleftharpoons} [Ru_3O(OAc)_6(CH_3OH)(H_2O)(OH)]$$

$$[Ru_3O(OAc)_6(CH_3OH)(H_2O)(OH)] \overset{-H^+}{\rightleftharpoons} [Ru_3O(OAc)_6(CH_3OH)(OH)_2]^-$$

The polarogram of the complex in methanol showed two reduction waves at $E_{\frac{1}{2}}$ = -0.20 V and $E_{\frac{1}{2}}$ = ca. -1.5 V. The separation $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ for the first wave at -0.20 V was consistent with a one-electron process. The second wave was irreversible, but its wave height was approximately twice that of the first wave, indicating a two-electron reduction. Thus the following reduction process was occurring —

$$Ru(III, III, III) \overset{+e}{\rightleftharpoons} Ru(III, III, II) \overset{+2e}{\longrightarrow} Ru(II, II, II)$$

The two complexes reacted with triphenylphosphine in methanol at room temperature to give methanol-insoluble products. $Ru_3O(OAc)_6(SO_2)(CH_3OH)_2$ gave the dark green complex $Ru_3O(OAc)_6(SO_2)(PPh_3)_2$ which showed a singlet in $CDCl_3$ at τ 10.08 for the resonance of the acetate groups. The two types of acetate thus appeared to coincide in their chemical shifts. The molecular weight (chloroform) indicated a trinuclear structure was correct. The polarogram in acetone showed two irreversible reduction waves at approximately $E_{\frac{1}{2}}$ = -1.14 V and $E_{\frac{1}{2}}$ = -1.48 V, the wave heights being roughly equal. It is likely that Ru(III, III, II) was reduced to Ru(II, II, II) in two one-electron steps.

$[Ru_3O(OAc)_6(CH_3OH)(H_2O)_2]_2(SO_4)$ gave the yellow-green complex $[Ru_3O(OAc)_6(PPh_3)_2(H_2O)]_2(SO_4)$, which showed a singlet for the acetate proton resonances at τ 10.08 ($CDCl_3$). The two types of acetate again had the same chemical shifts, as in the complex, $Ru_3O(OAc)_6(SO_2)(PPh_3)_2$. The molecular weight in chloroform was about one third of the calculated value, suggesting the complex was ionic or was dissociating. The polarogram in acetone showed three very

irreversible reduction waves at $E_{\frac{1}{2}}$ = -0.76 V, -1.06 V, and -1.36 V approximately. No determinations of the number of electrons involved could be made by the polarographic method, but it is reasonable to assume that Ru (III, III, III) was reduced in three one-electron steps to Ru(II, II, II).

$Ru_3O(OAc)_6(SO_2)(CH_3OH)_2$ and $[Ru_3O(OAc)_6(CH_3OH)(H_2O)_2]_2(SO_4)$ both gave $Ru_3O(OAc)_6(PPh_3)_3$ when heated under reflux with triphenyl phosphine in methanol.

COMPLEXES WITH TRIPHENYLPHOSPHITE.

The light green acetate, $Ru_3O(OAc)_6(H_2O)_3$, reacted with triphenylphosphite in methanol to give a deep blue solution from which the complex $Ru_3O(OAc)_6(P(OPh)_3)(H_2O)_2$ was isolated as a dark blue solid. The same product was given using $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ as starting material. The complex was soluble in methanol, benzene and chloroform, and almost insoluble in water. A molecular weight determination in chloroform indicated a trinuclear structure.

High voltage paper electrophoresis showed the presence of coordinated water molecules in the compound. In an acidic medium (pH 1.8) and in a neutral medium, the complex remained stationary, indicating an uncharged species. In a basic medium (pH 9.2) the complex migrated as an anion, one water molecule losing a proton to form a hydroxyl ion. The polarogram of the complex in acetone showed very irreversible reduction waves and no conclusions on the processes involved could be made.

The ^1H n.m.r. spectrum of $Ru_3O(OAc)_6(P(OPh)_3)(H_2O)_2$ in $CDCl_3$ showed very broad peaks, indicating the complex was probably paramagnetic. The triphenylphosphite protons occurred at τ 2.8, the protons of coordinated water at τ 6.1 and the acetate protons at τ 6.7 and τ 7.8, ratios approximately 1:2. These were due to the two acetate groups adjacent to two water molecules and the four acetate groups adjacent to the phosphite, respectively. The magnetic moment was 2.00 B.M., indicating that a slight amount of spin-spin interaction *via* the central oxygen atom was occurring in this Ru(III, III, II) complex.

The triphenylphosphite complex, $Ru_3O(OAc)_6(P(OPh)_3)(H_2O)_2$, reacted slowly with triphenylphosphine in methanol to give a green solution from which green crystals of $Ru_3O(OAc)_6(P(OPh)_3)_2(PPh_3)$

slowly separated on standing. A molecular weight determination in chloroform indicated a trinuclear structure. The complex was soluble in chloroform and benzene, and insoluble in methanol and water. The microanalytical figures fitted the above formulation rather than the expected product, $Ru_3O(OAc)_6(P(OPh)_3)(PPh_3)_2$. The low yield of the product suggested that it was probably formed by some dissociative process.

The polarogram in acetone showed an oxidation wave attributable to triphenylphosphine and an irreversible reduction wave at $E_{\frac{1}{2}}$ = -1.08 V. The polarogram was very similar to that of the triphenylphosphine complex, $Ru_3O(OAc)_6(PPh_3)_3$, which undergoes a two-electron reduction. The process is irreversible, the Ru(III, III, II) complex breaking up to give the mononuclear species $Ru(II)(OAc)_2(PPh_3).nCH_3OH$ [17]. It is likely that a similar two-electron reduction process occurred in the triphenylphosphite complex, accounting for the irreversibility of the reduction wave.

The n.m.r. spectrum of $Ru_3O(OAc)_6(P(OPh)_3)_2(PPh_3)$ in $CDCl_3$ showed the phenyl protons resonating as a broad multiplet at τ 2.0 - 2.4 and the acetate protons as a singlet at τ 9.93. The two types of acetate in the complex thus appeared to have the same chemical shift.

COMPLEXES WITH DIALKYLDITHIOCARBAMATES.

The dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, reacted with sodium diethyldithiocarbamate in methanol to give a dark brown precipitate and an orange-brown solution. The precipitate was recrystallised to give dark brown lustrous crystals of $Ru(S_2C.NEt_2)_3$. The solution was chromatographed on alumina and orange-brown crystals of the complex, $Ru_3O(S_2C.NEt_2)_6(OAc)(H_2O)_2$, were isolated from the main fraction.

The complex, $Ru(S_2C.NEt_2)_3$, was first prepared by Malatesta [21] from K_2RuCl_6 and from ruthenium trichloride with sodium diethyldithiocarbamate. The complex was reported to be difficult to crystallise [21], but dark lustrous crystals were obtained and an X-ray crystallographic analysis of these [22] showed the complex to have three bidentate dithiocarbamate groups (Figure 6). —

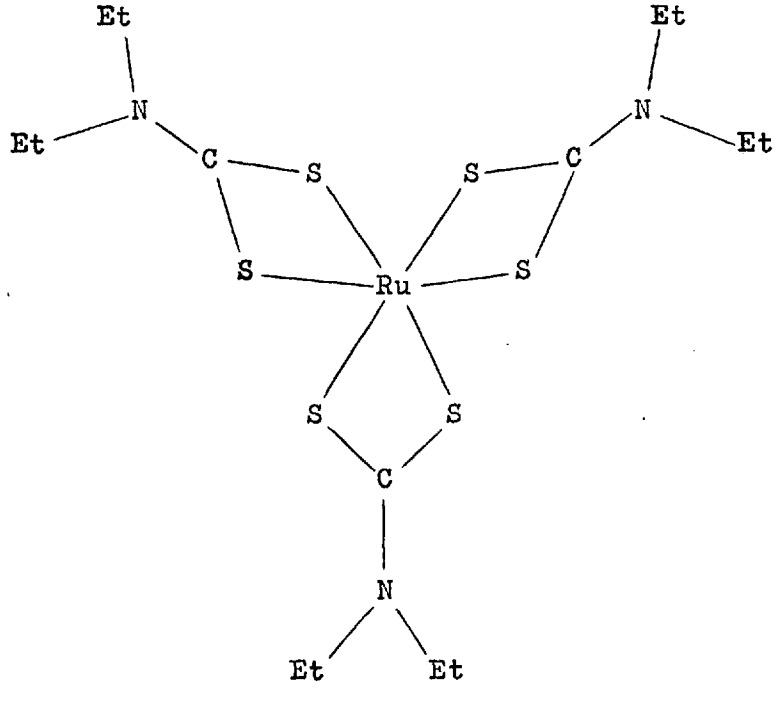


Figure 6.

The preparation using commercial ruthenium trichloride was repeated with slight modifications and the same product $Ru(S_2C.NEt_2)_3$ was readily obtained as large dark brown crystals.

The magnetic moment of the complex prepared from $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ was 2.05 B.M., a value comparable with the magnetic moments of other ruthenium (III) complexes [23]. A molecular weight determination in chloroform confirmed the mononuclear structure.

The n.m.r. spectrum of the complex, $Ru(S_2C.NEt_2)_3$, showed at 30°C only one rather broad peak at τ 9.2. At -55°C however, two broad peaks were observed at τ 6.15 and τ 8.65 in the approximate ratios 2:3 . These were due to the methylene and methyl proton resonances respectively of the ethyl groups of the dithiocarbamate ligands. The proton-proton coupling patterns could not be resolved, and this was probably partly due to the paramagnetism of the complex. The resonances of the methylene and methyl protons in sodium diethyldithiocarbamate occur as a quartet at τ 5.90 and a triplet at τ 8.78 respectively. At 30°C some kind of rapid exchange process was probably occurring in the complex, resulting in broadening of the peaks to such an extent that the resonance of the methylene protons was too broad to be observed. At -55°C such exchange processes occur at a much slower rate. Thus two separate, but still broad resonances were observed for the CH_2 and CH_3 protons of the ethyl groups.

The polarogram of $Ru(S_2C.NEt_2)_3$ in acetone showed an oxidation wave at $E_{\frac{1}{2}}$ = +0.28 V and a reduction wave at $E_{\frac{1}{2}}$ = -0.93 V. The two waves were of similar heights and the separations of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ were consistent with reversible one-electron processes for each wave. The following redox reactions thus seem likely —

$$\text{Ru(IV)} \underset{+0.28\text{V}}{\overset{-e}{\rightleftharpoons}} \text{Ru(III)} \underset{-0.93\text{V}}{\overset{+e}{\rightleftharpoons}} \text{Ru(II)}$$

The polarogram is shown in Figure 7.

Polarogram of $Ru(S_2C.NEt_2)_3$. (Acetone solution.)

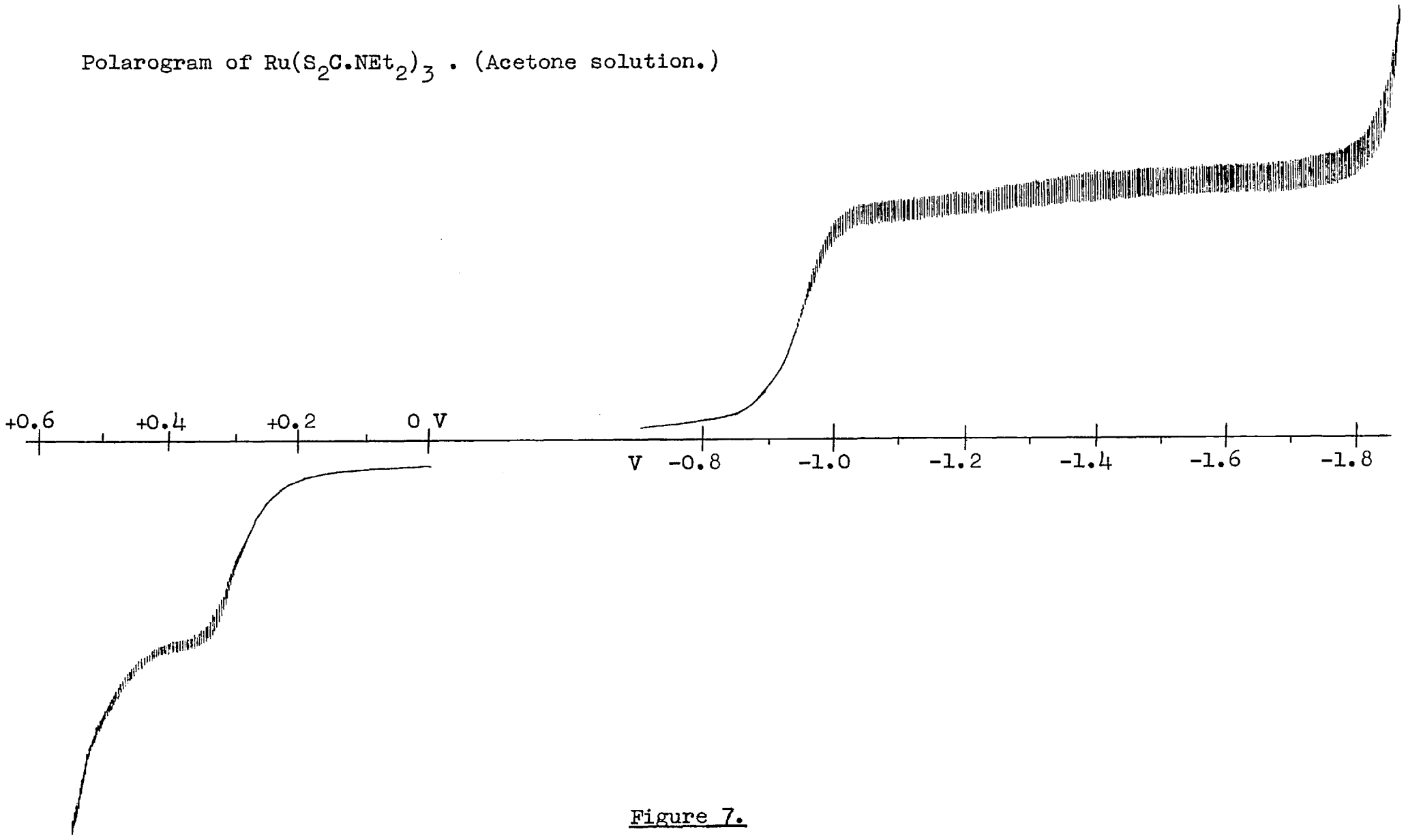


Figure 7.

The main methanol-soluble product of the reaction of $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ with sodium diethyldithiocarbamate was the orange-brown complex, $Ru_3O(S_2C.NEt_2)_6(OAc)(H_2O)_2$. A molecular weight determination in chloroform verified the trinuclear structure. Thus the diethyldithiocarbamate groups had displaced the acetate groups to give a novel Ru_3O complex with bridging dithiocarbamate groups, Figure 8.

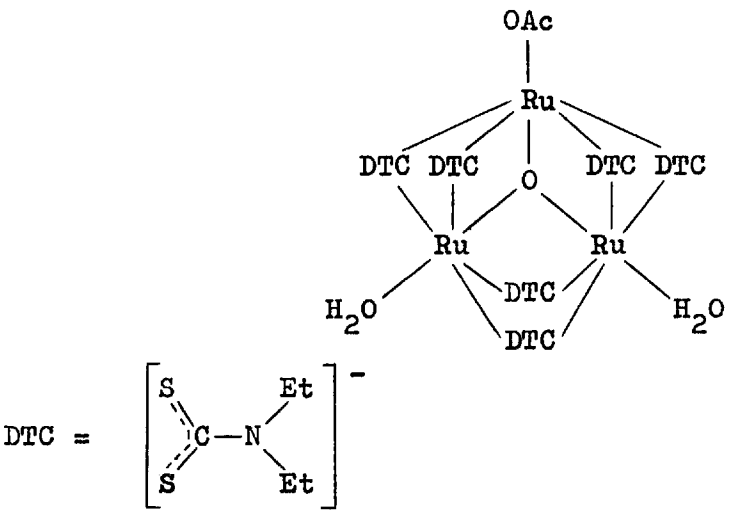


Figure 8.

The n.m.r. spectrum of the complex in $CDCl_3$ showed the methyl protons of the diethyldithiocarbamate groups as a multiplet at τ 8.82 and the methylene protons as a multiplet at τ 6.18. The acetate protons occurred as a singlet at τ 8.25 and the water protons as a broad peak at τ 6.68. The multiplicity of the resonances of the methyl and methylene protons of the diethyldithiocarbamate groups was due to the overlap of the resonances of the four dithiocarbamate groups adjacent to the acetate group and the two dithiocarbamate groups adjacent to the two water molecules. Further complexity was induced by the non-equivalence of the two ethyl groups in each dithiocarbamate bridge.

The polarogram of the complex in acetone showed a very

irreversible reduction wave. The magnetic moment of the complex, $Ru_3O(S_2C.NEt_2)_6(OAc)(H_2O)_2$, was 1.80 B.M., a value consistent with a $Ru(III)_3O$ unit in which marked spin-spin interaction would be expected *via* the central oxygen atom.

The triphenylphosphine complex, $Ru_3O(OAc)_6(PPh_3)_3$, reacted with sodium diethyldithiocarbamate in boiling methanol to give a brown precipitate which was recrystallised to give the complex, $[Ru(S_2C.NEt_2)_2(OAc)]_2$. The molecular weight determination in chloroform indicated that the complex was dimeric.

The n.m.r. spectrum of the complex in $CDCl_3$ showed the methyl protons of the diethyldithiocarbamate groups occurring as a broad multiplet centred at τ 8.70 and the methylene protons as two broad overlapping multiplets centred at τ6.02 and τ6.38. The acetate protons occurred as a broad peak at τ 8.00. The complexity of the resonances of the diethyldithiocarbamate protons indicated that the two ethyl groups in each dithiocarbamate group were non-equivalent and that probably the dithiocarbamate groups were non-equivalent also.

The complex was found to be slightly paramagnetic with μ_{eff} = 0.49 B.M. *per* Ru_2 unit. This very low value for a Ru(III, III) complex suggested that the compound perhaps had a Ru-Ru bond *via* which spin-spin interaction occurred. Thus several structures may be postulated for the complex, $[Ru(S_2C.NEt_2)_2(OAc)]_2$, some examples being given in Figure 9.

Compound II) would seem the most likely from the complexity of the n.m.r. spectrum, since it contains three different types of dithiocarbamate group: two non-equivalent bridging groups and two equivalent monodentate groups. Compounds I) and III) contain only two different types of dithiocarbamate group, and are therefore less likely. Compound IV) is also less likely, although of the type with four bridging ligands which is frequently found in ruthenium

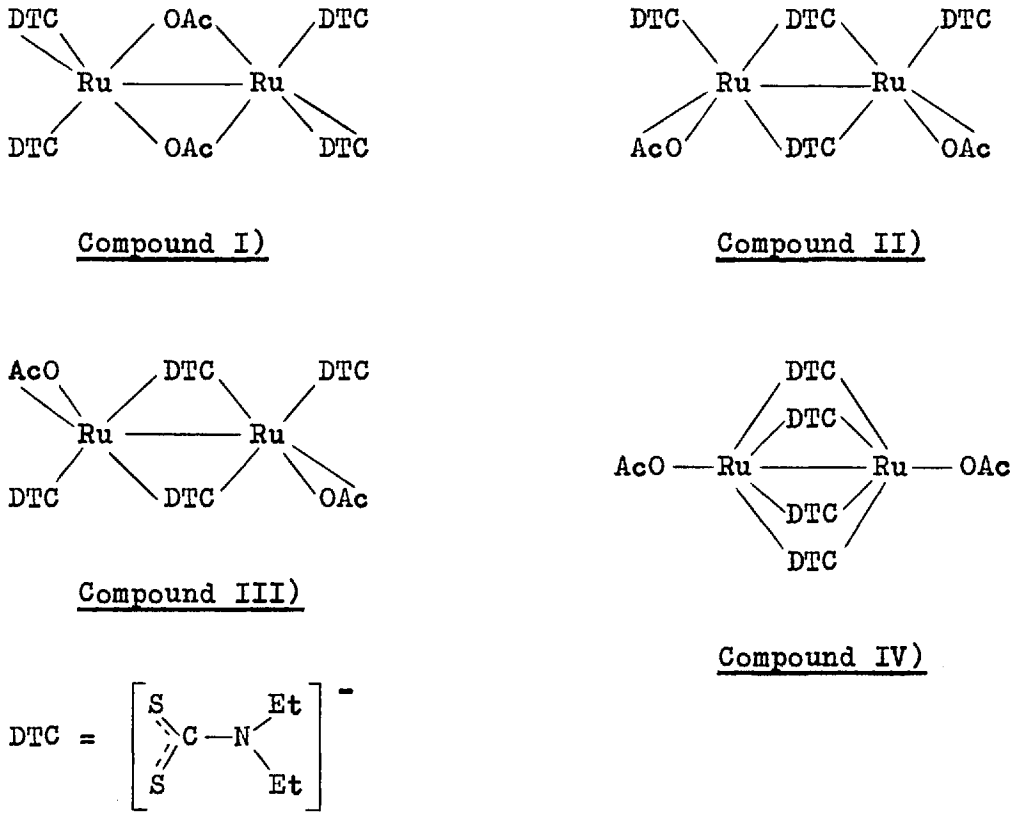


Figure 9.

chemistry [2,17]. All four bridging dithiocarbamate groups are equivalent and would give a relatively simple n.m.r. spectrum.

The non-equivalence of the two alkyl groups in a bidentate dithiocarbamate group is due to hindered rotation about the carbon-nitrogen bond which has partial π-character. This has been demonstrated in studies of the complex, $Ru(NO)(S_2C.NMe_2)_3$, which has been shown by X-ray analysis [22] to be six-coordinate, with two bidentate and one monodentate dithiocarbamate groups. The n.m.r. spectrum showed five peaks in the ratios 2:1:1:1:1 [24]. The peaks of relative intensity 1 were due to the four non-equivalent methyl groups of the two bidentate ligands, where rotation about the C-N bond was resticted because of bond multiplicity. For the monodentate ligand, where the C-N bond order was presumably one and free rotation could occur, only one methyl resonance of relative intensity 2 was observed. Analogous results have been observed for mono-and di-nitrosyl

dithiocarbamato complexes of molybdenum and tungsten, and for the rhodium complex, $Rh(S_2C.NMe_2)_3(PPh_3)$ [25].

The polarogram of $[Ru(S_2C.NEt_2)_2(OAc)]_2$ in acetone showed two reduction waves at $E_{\frac{1}{2}}$ = -0.58 V and $E_{\frac{1}{2}}$ = ca. -1.0 V, the latter being very irreversible. The wave heights were roughly equal, and the separation of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ for the first wave at -0.58 V was consistent with a one-electron reduction process. Thus the following reductions were probably taking place —

$$\text{Ru(III, III)} \overset{+e}{\rightleftharpoons} \text{Ru(III, II)} \overset{+e}{\longrightarrow} \text{Ru(II, II)}$$

The dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, similarly reacted with sodium dimethyldithiocarbamate in methanol to give a dark brown precipitate and an orange-brown solution. Dark brown lustrous crystals of $Ru(S_2C.NMe_2)_3$ [21] were obtained from the precipitate, and orange-brown crystals of $[Ru(S_2C.NMe_2)_2(OH)]_2$ from the solution after chromatography on alumina.

The polarogram of $Ru(S_2C.NMe_2)_3$ in acetone was very similar to that of the diethyl analogue (Figure 7), with an oxidation wave at $E_{\frac{1}{2}}$ = +0.32 V and a reduction wave at $E_{\frac{1}{2}}$ = -0.90 V. The separations $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ were consistent with reversible one-electron processes occurring in both cases, and similar reactions are proposed —

$$\text{Ru(IV)} \underset{+0.32\text{V}}{\overset{-e}{\rightleftharpoons}} \text{Ru(III)} \underset{-0.90\text{V}}{\overset{+e}{\rightleftharpoons}} \text{Ru(II)}$$

The magnetic moment of the complex, μ_{eff}, was 2.00 B.M., agreeing with values for other Ru(III) complexes [23]. The n.m.r. spectrum in $CDCl_3$ showed a single sharp resonance at τ 9.98 for the methyls of the dithiocarbamate groups.

The orange-brown complex, $[Ru(S_2C.NMe_2)_2(OH)]_2$, was shown to be dimeric by a molecular weight determination in chloroform. The n.m.r. spectrum ($CDCl_3$) showed a multiplet at τ 6.43 consisting

roughly of four peaks, intensity ratios 2:2:1:1 and two peaks (1:1) at τ 6.80. These were due to the methyl protons of the dithiocarbamate ligands, and the complexity of the n.m.r. spectrum indicated that these ligands were non-equivalent. The hydroxyl protons occurred as a broad singlet at τ 8.05. The complex was slightly paramagnetic with μ_{eff} = 0.4 B.M. per Ru_2 unit. This very low value for a Ru(III, III) complex suggested that the compound probably had a Ru-Ru bond, as in $[Ru(S_2C.NEt_2)_2(OAc)]_2$. A possible stucture for $[Ru(S_2C.NMe_2)_2(OH)]_2$ is illustrated in Figure 10. —

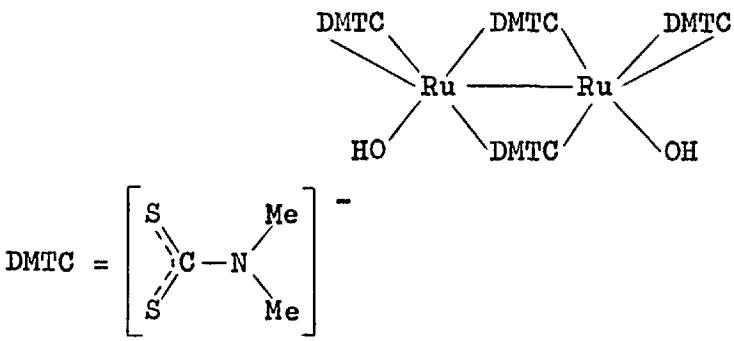


Figure 10.

The two chelated dithiocarbamate groups were equivalent and gave rise to the two peaks of intensity ratio 2:2 in the n.m.r. The two bridging dithiocarbamate groups were non-equivalent and gave rise to four methyl peaks, intensity ratios 1:1:1:1. Non-equivalence of the two methyl groups in each dithiocarbamate ligand was caused by hindered rotation about the carbon-nitrogen bond as described previously [24].

The polarogram of $[Ru(S_2C.NMe_2)_2(OH)]_2$ in acetone showed two very irreversible reduction waves at $E_{\frac{1}{2}}$ = -0.58 V and $E_{\frac{1}{2}}$ = ca. -1.0 V. Reduction of Ru(III, III) to Ru(II, II) via two irreversible one-electron steps was probably occurring.

2-MERCAPTOBENZTHIAZOLE COMPLEX.

The dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, reacted with 2-mercaptobenzthiazole in boiling methanol to give a dark brown precipitate from which brown crystals of $Ru(S_2NC_7H_4)_2(OAc)$ were obtained. The molecular weight in chloroform indicated a mononuclear structure as shown in Figure 11.

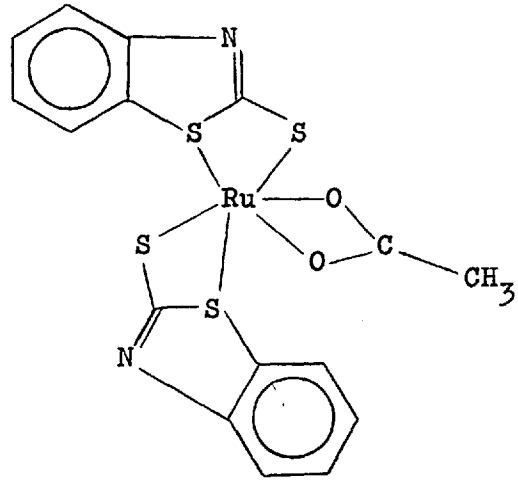


Figure 11.

The magnetic moment was 1.36 B.M., a rather low value for a mononuclear Ru(III) complex. The polarogram in acetone showed a highly irreversible reduction process occurring.

DIPHENYLDITHIOPHOSPHATE COMPLEX.

The dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, reacted with diphenyldithiophosphoric acid in methanol to give a dark red precipitate which was purified by chromatography on alumina to give dark pink crystals of $Ru(S_2PPh_2)_3$. The crystals were fairly stable in the solid state, but decomposed quite readily in solutions exposed to air, turning brown. The molecular weight determination in chloroform, excluding oxygen, indicated a mononuclear structure.

The n.m.r. spectrum in $CDCl_3$ showed the phenyl protons as mutiplets at τ 2.10 and τ 2.45. The magnetic moment was 1.95 B.M., a normal value for Ru(III) complexes [23]. The polarogram in acetone showed a very irreversible reduction process occurring.

EXPERIMENTAL.

Elemental analyses were by the Microanalytical Laboratory, Imperial College. N.m.r. spectra were recorded on Perkin-Elmer R12 (60 MHz) and R14 (100 MHz) spectrometers and i.r. spectra on Perkin-Elmer 257 and 457 instruments. Molecular weights were determined on a Hitachi Perkin-Elmer Model 115 instrument. A Camag High Voltage Electrophoresis apparatus was used for the electrophoretic studies. Polarography and controlled potential electrolysis were carried out using a Beckmann Electroscan $^{TM}30$ polarograph.

Ruthenium trichloride trihydrate was from Johnson Matthey Limited. Other reagents were AnalaR Grade.
Chromatography was carried out using acid-washed alumina (Spencer Chemicals for Industry, Type H) and Sephadex (Grade G10).
Infra-red spectra were run as Nujol mulls using sodium chloride plates, unless otherwise stated.

Electrophoresis. — High voltage paper electrophoresis was carried out at 2 kV. Formic acid - acetic acid buffer (27 and 75 ml per litre respectively, pH 1.8), potassium dihydrogen orthophosphate and dipotassium hydrogen orthophosphate buffer (0.025 M in each, pH 7.0), and sodium borate buffer (0.05 M, pH 9.2) were used for acidic, neutral and alkaline experiments, respectively.

Electrochemistry. — Polarography and controlled potential electrolysis were carried out in conventional H-cells. All solutions were deoxygenated by nitrogen, purified by passage through a chromous solution and two bubblers of the organic solvent.
A conventional dropping mercury electrode and a rotating platinum

electrode were used for polarographic studies and all controlled potential electrolyses were performed at a mercury pool. The anode was of platinum foil in a 0.1M aqueous solution of the supporting electrolyte, separated from the ruthenium solutions by a 3% agar bridge. AnalaR $NaClO_4$, dried at 80°C under vacuum, was used as the supporting electrolyte. An aqueous S.C.E. in contact with a 0.1M aqueous $NaClO_4$ solution separated from the ruthenium solution by an agar bridge was used as reference electrode. Concentrations were in the range 10^{-3} to 10^{-4}M, made up in acetone, methanol, tetrahydrofuran or dimethylformamide.

Magnetic Moments. — These were measured for solid samples on a refined version [26] of the Evans simplification of the Gouy-Rankine Balance [27].

Starting Materials. — $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, $[Ru_3O(OAc)_6(py)_3]Cl$, and $Ru_3O(OAc)_6(PPh_3)_3$ were prepared by the methods described in the literature [3]. Reductions of $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ to the complexes $Ru_3O(OAc)_6(H_2O)_3$ and $Ru_3(OAc)_6(H_2O)_3$ were carried out in glass pressure bottles (Fisher and Porter 8 oz Compatibility Bottles) with hydrogen at two atmospheres pressure, using Adams catalyst (PtO_2) [3].

Monocarbonylbis(methanol)hexa-μ-acetato-μ_3-oxo-triruthenium(III, III, II). — The aquo-acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ [3], (0.5g, 0.63mmol) was dissolved in methanol (5ml) and reduced with hydrogen to the light green acetate, $Ru_3O(OAc)_6(H_2O)_3$ [3]. This was stirred under carbon monoxide (2 atm.) for 30 min. The purple solution was evaporated to low volume and chromatographed on Sephadex in water. The main purple fraction was evaporated to dryness and the solid residue was crystallised from methanol to give purple crystals of the carbonyl

complex (0.40g, 80% yield). (Found : C, 23.6; H, 3.7; M, 744 (CH_3OH), 762 (H_2O). $C_{15}H_{26}O_{16}Ru_3$ requires C, 23.5; H, 3.4% ; M, 767).
The carbonyl complex was also obtained by the same method from the fully reduced yellow species, $Ru_3(OAc)_6(H_2O)_3$ [3], and from the original dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ [3], the latter complex requiring 24 hr for complete reaction.

Monocarbonylbis(pyridine)hexa-μ-acetato-μ_3-oxo-triruthenium(III, -III, II). —— i) The purple carbonyl complex, $Ru_3O(OAc)_6(CO)(CH_3OH)_2$, (0.2g, 0.26mmol) was dissolved in methanol (3ml) and pyridine (0.5ml) was added. The mixture was warmed on a steam bath for 10 min and then allowed to cool slowly. The dark blue crystals formed were filtered off and recrystallised from chloroform to give the carbonyl complex, (0.13g, 60% yield). (Found : C, 31.9; H, 3.7; N, 3.3; M, 823 ($CHCl_3$). $C_{23}H_{28}N_2O_{14}Ru_3$ requires C, 32.1; H, 3.3; N, 3.3% ; M, 861).
ii) The pyridine complex, $[Ru_3O(OAc)_6(py)_3]Cl$ [3], (0.2g, 0.21mmol) was dissolved in methanol (10ml) and heated under reflux. Carbon monoxide was bubbled through the boiling solution for 4 hr. On cooling, dark blue crystals were precipitated. Recrystallisation of these from chloroform gave the carbonyl complex, (0.07g, 40% yield).
iii) The pyridine complex, $[Ru_3O(OAc)_6(py)_3]Cl$ [3], (0.2g, 0.21mmol) was dissolved in methanol (5ml) and stirred under carbon monoxide (2 atm.) for 24 hr. The dark blue crystals formed were recrystallised from chloroform to give the carbonyl complex, (0.04g, 20% yield).

Tetra-μ-acetatomonocarbonyltriphenylphosphinediruthenium(II). —— The purple carbonyl complex, $Ru_3O(OAc)_6(CO)(CH_3OH)_2$, (0.2g, 0.26mmol) and triphenylphosphine (0.13g, 0.52mmol) were dissolved in methanol (10ml) and stirred under nitrogen for 4 hr. The turquoise solid formed was filtered off and chromatographed on alumina in chloroform.

The main fraction was evaporated to low volume to give turquoise crystals of the binuclear complex, (0.09g, 50% yield). (Found : C, 44.9; H, 3.6; P, 5.3; M, 492 ($CHCl_3$). $C_{27}H_{27}O_9PRu_2$ requires C, 44.5; H, 3.7; P, 4.3% ; M, 730).

catena-Di-μ-acetatodicarbonylruthenium.[18] — Commercial ruthenium trichloride (0.5g) was dissolved in ethanol (10ml) and stirred under carbon monoxide (2 atm.) for 3 days. The yellow solution was evaporated to give a crude yellow-brown solid. This was redissolved in ethanol (13ml) and sodium acetate (1g) and glacial acetic acid (13ml) were added [3]. The mixture was heated under reflux for 4 hr. The precipitate formed was filtered off and washed with water and ethanol to give the polymeric carbonyl complex as an orange-yellow amorphous solid, (0.35g, 70% yield), ν_{CO} 2045m, 1990s, 1960s, 1950s cm^{-1}. (Found : C, 22.3; H, 1.4. $(C_4H_3O_4Ru)_n$ requires C, 22.1; H, 1.4%).

Di-μ-acetatotetracarbonylbis(triphenylphosphine)diruthenium.[18] — The polymeric carbonyl complex, $[Ru(CO)_2(OAc)]_n$, (0.15g) and triphenyl phosphine (0.30g, excess) were heated in boiling chloroform till all the polymer had dissolved. The resulting solution was evaporated to dryness and the solid residue was washed with diethylether and recrystallised from chloroform to give yellow crystals of the dimeric carbonyl complex, (0.24g, 80% yield), ν_{CO} 2015s, 1975m, 1940s, 1910w cm^{-1}, τ ($CDCl_3$) 2.32 (6H,m), 2.46 (9H,m), 8.32 (3H,s). (Found : C, 55.9; H, 4.0; P, 5.9. $C_{44}H_{36}O_8P_2Ru_2$ requires C, 55.2; H, 3.8; P, 6.5%).

Dinitrosylhydroxohexa-μ-acetato-μ_3-oxo-triruthenium(III, II, II). — Nitric oxide was bubbled through a solution of the light green reduced acetate, $Ru_3O(OAc)_6(H_2O)_3$ [3], (0.46g, 0.63mmol) in methanol (10ml) for 30 min. The brown solution was evaporated to dryness and the solid was

chromatographed on alumina in chloroform. The main brown fraction was evaporated to a low volume to give brown crystals of the nitrosyl complex, (0.38g, 80% yield). (Found : C, 19.5; H, 2.7; N, 3.6; M, 721 ($CHCl_3$). $C_{12}H_{19}N_2O_{16}Ru_3$ requires C, 19.2; H, 2.5; N, 3.7% ; M, 752). The nitrosyl complex was also prepared by the same method from the dark green complex, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ and the yellow fully-reduced complex, $Ru_3(OAc)_6(H_2O)_3$.

Monosulphonylbis(methanol)hexa-μ-acetato-μ_3-oxo-triruthenium(III, III II) and bis[di(aquo)methanolhexa-μ-acetato-μ_3-oxo-triruthenium(III, III, III)]sulphate. —— Sulphur dioxide was bubbled into a solution of the light green acetate, $Ru_3O(OAc)_6(H_2O)_3$ [3], (0.46g, 0.63mmol) in methanol (10ml) for 1 hr. The deep blue solution was evaporated to a low volume and chromatographed on Sephadex in water. The first dark blue fraction was evaporated to dryness and recrystallised from methanol to give dark blue crystals of the sulphonyl complex, (0.20g, 40% yield). (Found : C, 20.1; H, 3.9; S, 3.3. $C_{14}H_{26}O_{17}Ru_3S$ requires C, 20.9; H, 3.2; S, 3.9%).

The second blue-green fraction was evaporated to dryness and recrystallised from methanol to give dark blue-green crystals of the sulphate complex, (0.20g, 40% yield). (Found : C, 19.7; H, 3.7; S, 1.8. $C_{26}H_{52}O_{36}Ru_6S$ requires C, 19.7; H, 3.3; S, 2.0%).

Monosulphonylbis(triphenylphosphine)hexa-μ-acetato-μ_3-oxo-triruthenium (III, III, II). —— The sulphonyl complex, $Ru_3O(OAc)_6(SO_2)(CH_3OH)_2$, (o.16g, 0.2mmol) and triphenylphosphine (0.16g, 0.6mmol) were dissolved in methanol (10ml) and stirred at room temperature for 12 hr. The green precipitate formed was filtered off and chromatographed on alumina in chloroform. The main fraction was evaporated to low volume to give dark green crystals of the sulphonyl complex, (0.15g, 60% yield).

(Found : C, 45.9; H, 4.0; P, 5.0; S, 2.4; M, 1207 ($CHCl_3$). $C_{48}H_{48}O_{15}P_2Ru_3S$ requires C, 45.5; H, 3.8; P, 4.9; S, 2.5% ; M, 1263).

Bis[aquobis(triphenylphosphine)hexa-μ-acetato-μ_3-oxo-triruthenium-(III, III, III)]sulphate. —— The sulphate complex, $[Ru_3O(OAc)_6(CH_3OH)(H_2O)_2]_2(SO_4)$, (0.16g, 0.1mmol) and triphenylphosphine (0.16g, 0.6mmol) were dissolved in methanol (10ml) and stirred at room temperature for 12 hr. The green precipitate formed was filtered off and chromatographed on alumina in chloroform. The main fraction was evaporated to dryness and the residue recrystallised from chloroform-diethyl ether to give yellow-green crystals of the sulphate complex, (0.13g, 50% yield). (Found : C, 45.6; H, 3.9; P, 4.9; S, 0.8; M, 909 ($CHCl_3$). $C_{96}H_{100}O_{32}P_4Ru_6S$ requires C, 45.5; H, 4.0; P, 4.9: S, 1.3% ; M, 2532).

Reactions of monosulphonylbis(methanol)hexa-μ-acetato-μ_3-oxo-triruthenium and bis[di(aquo)methanolhexa-μ-acetato-μ_3-oxo-triruthenium] sulphate with triphenylphosphine in boiling methanol. ——

i) The sulphonyl complex, $Ru_3O(OAc)_6(SO_2)(CH_3OH)_2$, (0.1g, 0.12mmol) and triphenylphosphine (0.09g, 0.36mmol) were heated under reflux in methanol (10ml) for 2 hr. Yellow-green crystals of the triphenylphosphine complex, $Ru_3O(OAc)_6(PPh_3)_3$, were isolated. (Found : C, 53.8; H, 4.4; P, 6.9. $C_{66}H_{63}O_{13}P_3Ru_3$ requires C, 54.2; H, 4.3; P, 6.4%).

ii) The sulphate complex, $[Ru_3O(OAc)_6(CH_3OH)(H_2O)_2]_2(SO_4)$, reacted similarly to give $Ru_3O(OAc)_6(PPh_3)_3$.

Bis(aquo)triphenylphosphitohexa-μ-acetato-μ_3-oxo-triruthenium(III, III, II). —— The light green acetate, $Ru_3O(OAc)_6(H_2O)_3{}^3$, (0.46g, 0.63mmol) was dissolved in methanol (10ml) and triphenylphosphite (0.6g, 2mmol) was added. The mixture was stirred for 12 hr and the solvent was removed. The oily residue was chromatographed on alumina

in chloroform. The main blue fraction was evaporated to low volume to give dark blue crystals of the triphenylphosphite complex, (0.45g, 70% yield). (Found : C, 35.8; H, 4.0; P, 3.1; M, 902 ($CHCl_3$). $C_{30}H_{37}O_{18}PRu_3$ requires C, 35.3; H, 3.6; P, 3.0% ; M, 1021).
The triphenylphosphite complex was similarly prepared from the dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$.

Triphenylphosphinebis(triphenylphosphito)hexa-μ-acetato-μ_3-oxo-triruthenium (III, III, II). —— The triphenylphosphite complex, $Ru_3O(OAc)_6(P(OPh)_3)(H_2O)_2$, (0.2g, 0.2mmol) and triphenylphosphine (0.16g 0.6mmol) were dissolved in methanol (10ml) and stirred for 12 hr. Green crystals slowly came out of the solution and were filtered off and chromatographed on alumina in chloroform. The main green fraction was evaporated to low volume giving bright green crystals of the bisphosphite complex, (0.09g, 30% yield). (Found : C, 50.5; H, 4.1; P, 6.6; M, 1500 ($CHCl_3$). $C_{66}H_{63}O_{19}P_3Ru_3$ requires C, 50.9; H, 4.1; P, 6.0% ; M, 1557).

Tris(diethyldithiocarbamato)ruthenium(III) [21] and acetatobis(aquo)-hexa-μ-diethyldithiocarbamato-μ_3-oxo-triruthenium(III, III, III). —— i) The dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$, (0.6g, 0.76mmol) and sodium diethyldithiocarbamate (1.54g, 6.8mmol) were dissolved in methanol (15ml) and stirred for 2 hr. The brown precipitate formed was filtered off and chromatographed on alumina in chloroform. The main fraction was evaporated to low volume to give dark brown lustrous crystals of tris(diethyldithiocarbamato)ruthenium, (0.62g, 50% yield). (Found : C, 33.2; H, 5.4; N, 7.8; S, 34.7; M, 538 ($CHCl_3$). $C_{15}H_{30}N_3RuS_6$ requires C, 33.0; H, 5.5; N, 7.7; S, 35.1% ; M, 546).
The orange-brown filtrate was chromatographed on alumina in chloroform. The main fraction was evaporated to dryness and recrystallised from

chloroform-diethyl ether to give orange-brown crystals of the trinuclear complex, (0.30g, 30% yield). (Found : C, 29.8; H, 4.8; N, 6.6; S, 30.6; M, 1290 ($CHCl_3$). $C_{32}H_{67}N_6O_5Ru_3S_{12}$ requires C, 29.4; H, 5.1; N, 6.4; S, 29.4% ; M, 1304).

ii) Commercial ruthenium trichloride (0.5g, 2mmol) and sodium diethyldithiocarbamate (1.35g, 6mmol) were dissolved in methanol (15ml) and stirred for 1 hr. The precipitate formed was chromatographed on alumina in chloroform. The main brown fraction was evaporated to low volume to give dark brown crystals of tris(diethyldithiocarbamato)-ruthenium, (0.77g, 70% yield).

Bis[acetatobis(diethyldithiocarbamato)ruthenium(III)]. — The triphenylphosphine complex, $Ru_3O(OAc)_6(PPh_3)_3$ [3], (0.3g, 0.2mmol) and sodium diethyldithiocarbamate (0.27g, 1.2mmol) were heated under reflux in methanol (15ml) for 4 hr. The precipitate formed was filtered off and chromatographed on alumina in chloroform. The main fraction was evaporated to dryness and recrystallised from chloroform-diethyl ether to give brown crystals of the dimer, (0.21g, 75% yield). (Found : C, 31.7; H, 5.1; N, 6.3; S, 29.2; M, 953 ($CHCl_3$). $C_{24}H_{46}N_4O_4Ru_2S_8$ requires C, 31.5; H, 5.0; N, 6.1; S, 28.0% ; M, 914).

Tris(dimethyldithiocarbamato)ruthenium(III) [21] and bis[hydroxy-bis(dimethyldithiocarbamato)ruthenium(III)]. — The dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ [3], (0.5g, 0.63mmol) and sodium dimethyldithiocarbamate (1.2g, 5.7mmol) were dissolved in methanol (15ml) and stirred for 2 hr. The brown precipitate was filtered off and chromatographed on alumina in chloroform. The main fraction was evaporated to low volume to give dark brown shiny crystals of tris(dimethyldithiocarbamato)ruthenium, (0.53g, 60% yield). (Found : C, 23.5; H, 3.9; N, 8.6; S, 40.6. $C_9H_{18}N_3RuS_6$ requires C, 23.4; H, 3.9; N, 9.1; S, 41.6%).

The orange-brown filtrate was chromatographed on alumina in chloroform and the main fraction was evaporated to dryness and recrystallised from chloroform-diethyl ether to give orange-brown crystals of the dimer, (0.13g, 20% yield). (Found : C, 19.6; H, 3.6; N, 7.6; S, 36.6; M, 689 ($CHCl_3$). $C_{12}H_{26}N_4O_2Ru_2S_8$ requires C, 20.0; H, 3.6; N, 7.8; S, 35.7% ; M, 718).

Acetatobis(2-mercaptobenzthiazolo)ruthenium(III). —— The dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ [3], (0.3g, 0.38mmol) and 2-mercaptobenzthiazole (0.57g, 3.42mmol) were dissolved in methanol (15ml) and heated under reflux for 4 hr. The dark brown solid formed was filtered off and recrystallised from chloroform-diethyl ether to give brown crystals of the mercaptobenzthiazole complex, (0.29g, 50% yield). (Found : C, 39.6; H, 2.7; N, 5.5; S, 25.3; M, 546 ($CHCl_3$). $C_{16}H_{11}N_2O_2RuS_4$ requires C, 39.0; H, 2.2; N, 5.7; S, 25.9% ; M, 493).

Tris(diphenyldithiophosphato)ruthenium(III). —— The dark green acetate, $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ [3], (0.4g, 0.51mmol) and diphenyldithiophosphoric acid (1.15g, 4.59mmol) were stirred together under nitrogen in methanol (10ml) for 3 hr. The dark red precipitate was filtered off and chromatographed on alumina in acetone. The main red fraction was evaporated to low volume under nitrogen to give dark pink crystals of tris(diphenyldithiophosphato)ruthenium, (0.65g, 50% yield). (Found : C, 50.7; H, 3.7; P, 11.1; S, 24.1; M, 869 ($CHCl_3$). $C_{36}H_{30}P_3RuS_6$ requires C, 50.9; H, 3.4; P, 11.0; S, 22.6% ; M, 849).

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