RHENIUM β-KETOENOLATE COMPLEXES

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by

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SCOPE AND CONTENTS:

The products of the reaction between oxomethoxodichlorobistriphenylphosphinerhenium(V) and acetylacetone are determined, characterized and correlated in terms of a reaction scheme. A series of rhenium(III) compounds, characteristic of reactions analogous to the one mentioned above, with other β-ketoenols is prepared and characterized. The syntheses and properties of tris-1,1,1-5,5,5-hexafluoropentane-2,4-dionatorhenium(III) and trispentane-2,4-dionatorhenium(III) are described. A new nitrido-rhenium complex, nitridochloro-1,1,1-5,5,5-hexafluoropentane-2,4-dionatobistriphenylphosphinerhenium(V) complex is prepared and characterized. A synthetic route to pyridine-acetylacetonate complexes of rhenium is described.

... to Diane and Ken

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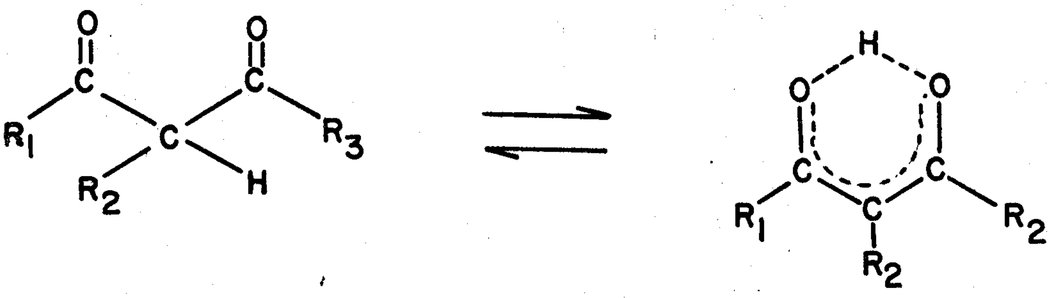
CHAPTER 1

INTRODUCTION

β-ketoenols, the ligands that "gave wings to the metals" (1), have been studied for more than a century. As the name implies, a significant feature of these ligands is keto-enol tautomerism.



keto form   enol form

Metal β-ketoenolates are formed when the enolic hydrogen is replaced by a metal ion. Bonding, therefore, occurs between the metal and the two oxygens of the β-ketoenolate anion giving a chelate, but this is not the only way in which these ligands may be bonded to metal ions. A sigma bond may be formed between the methylene carbon of the ligand anion and the metal (2). Moreover, a pi bonded system may exist in which the neutral ligand is involved in an allylic-type linkage to the metal (3). Bridging of two metal ions may be accomplished in two ways: 1) each of the ligand oxygens bonded to a different metal ion (4), 2) one of the oxygens of a chelated ligand bonded to a second metal ion as in Ni(II) and Co(II) acetylacetonates (5). Chelates may be formed by both the neutral ligand and the anion. In addition, combinations of the various types of bonding may exist in the same compound.

1. MOLECULAR STRUCTURES

Metal β-ketoenolates and metal complexes containing β-ketoenols, or β-ketoenolate anions as ligands may be grouped in two classes, - mononuclear species and polynuclear species.*

1.1. Mononuclear Species

Two idealized symmetry arrangements of ligand oxygen atoms are possible in four-coordinate metal β-ketoenolates in which the metal ions are bi-valent: tetrahedral and square planar (5). Octahedral arrays of oxygens are expected in six-coordinate metal β-ketoenolates of tri-valent metal ions. Tri or tetra-valent metal ions may give eight-coordinate metal β-ketoenolates in which the ligand oxygens are arranged in anti-prismatic or dodecahedral fashion (5).

Some mononuclear platinum complexes have been reported (2,3,6), which exhibit various types of bonding between the metal and the β-ketoenolate ligand. These compounds are depicted in FIGURE 1.

In the compound, pentane-2,4-dionatotrismethyldipyridylplatinum-(IV), $Pt(AA)(CH_3)_3dipy$**+, the methylene carbon atom of the acetylacetonate

---

* mononuclear or polynuclear with respect to the metal ion "nucleus".

** See Appendix for abbreviations.

\+ Compounds will be named according to the I.U.P.A.C. system and the formula given. After the first instance, the compound will be signified by the formula because the names are so long and cumbersome.

anion occupies an apical position in the coordination octahedron; the dipyridyl system is used to define the equatorial plane (6). The methylene carbon atom of one of the AA's in the compound potassium chlorobispentane-2,4-dionatoplatinum(II), $K[PtC\ell(AA)_2]$, occupies one coordination position in the square plane, while the oxygens from the second AA occupy two more (6). A square planar arrangement, of two oxygens from one AA and a methylene carbon from each of two more AA's, surrounds the platinum(II) ion in the compound potassium trispentane-2,4-dionatoplatinum(II), $K[Pt(AA)_3]$. In the compound sodium dichlorobispentane-2,4-dionatoplatinum(II) dihydrate, both AA's are bonded to the platinum(II) ion through the methylene carbons (6).

In the compound $HPt(AA)_2C\ell$ two coordination positions are occupied by a chelating AA, a third is taken up by $C\ell^-$ and the final coordination position is filled by an enol-form acetylacetone which is thought to be bonded in a manner similar to that in pi-allyl complexes (3).

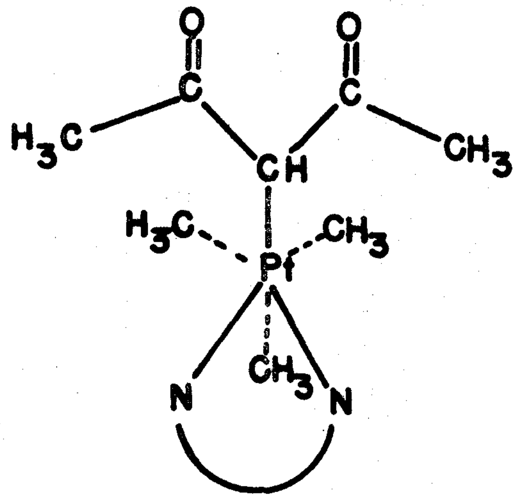
A notable aspect of the more common metal β-ketoenolate chelates is that the chelate rings are not completely planar. The dihedral angle between the plane of the O-M-O portion of the ring and the plane of the rest of the atoms in the ring varies from 0° (7) to 22° (8). This bending of the chelate ring has been attributed to intermolecular hydrogen bonding in the compound bispentane-2,4-dionatocobalt(II) dihydrate (7) and to inter-ring conjugation in the compound bispentane-2,4-dionatooxo vanadium(IV) (9).

1.2 Polymeric Species

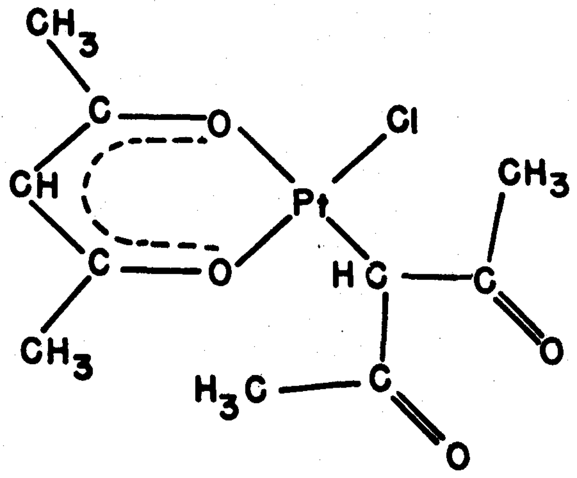
The discovery of the polymeric nature of bispentane-2,4-dionatonickel(II) trimer and the subsequent examination of other metal β-

FIGURE 1

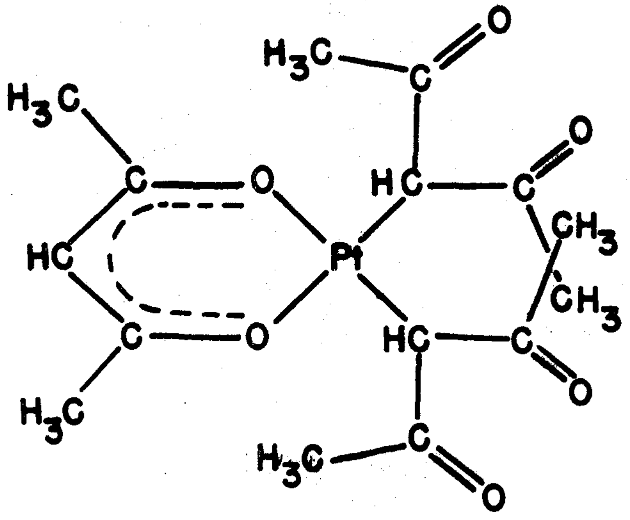
Examples of the various types of bonding found in metal β-ketoenolate complexes



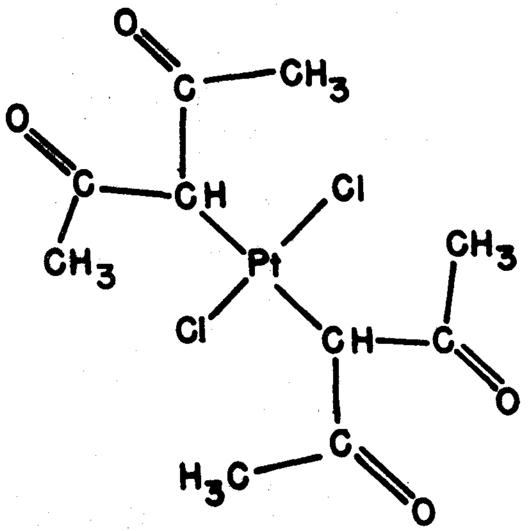
Pt AA $(CH_3)_3$ dipy



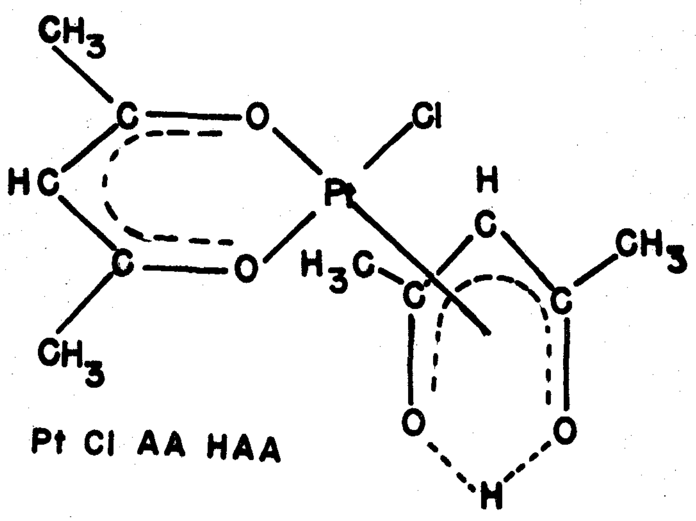
$K[PtCl(AA)_2]$



$K[Pt(AA)_3]$



$Na_2[PtCl_2(AA)_3]\cdot 2H_2O$



Pt Cl AA HAA

FIGURE: 1

ketoenolate complexes for such behaviour have prompted two postulates about polymeric species. Polymers may exist if the stereochemistry of the ligands will permit them and if the β-ketoenolate ligands leave the metal coordinatively unsaturated (5).

Three polymeric forms have been established; examples of these are depicted in FIGURE 2.

In the nickel and cobalt compounds, there is an octahedral arrangement of oxygen atoms about each metal ion. There is a pseudo-octahedral environment about each platinum in the platinum compound.

A fourth polymeric form, a dimer with bridging AA groups, was postulated for a rhenium(IV) compound (4), but this has been shown to be incorrect (10). The compound dichlorobispentane-2,4-dionatorhenium(IV) is monomeric in the solid state.

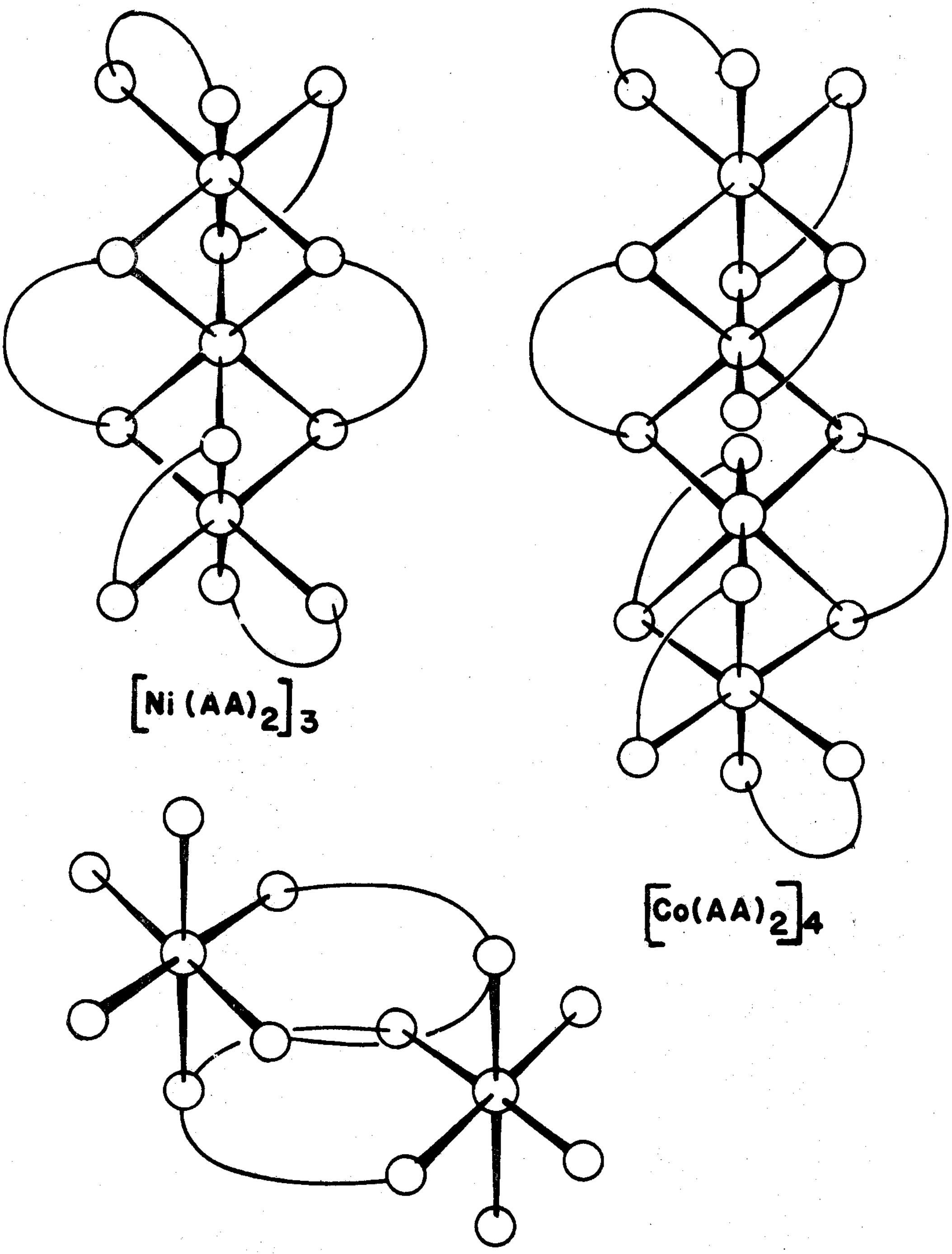
2. Rhenium β-ketoenolate Complexes

The first β-ketoenolate complex of rhenium to be reported was trispentane-2,4-dionatorhenium(III), $Re(AA)_3$ (11). It was described as a brown, paramagnetic compound obtained by reacting rhenium dioxide, ReO_2 or hydrated rhenium sesquioxide, $Re_2O_3 \cdot xH_2O$, with acetylacetone. More recently, tris1,1,1,5,5,5-hexafluoropentane-2,4-dionatorhenium(III) has been prepared by the destructive distillation of a finely ground mixture of rhenium trichloride, $Re_3C\ell_9$, and anhydrous sodium hexafluoroacetylacetonate, NaHFAA, in an argon atmosphere (12). The product, a dark purple vapor, gives dark purple crystals on cooling. Both the solid and the vapor seem quite resistant to air oxidation.

A series of compounds containing other ligands in addition to β-ketoenolate anions has been obtained by reacting oxoethoxodichloro-

FIGURE 2

Polymeric metal β-ketoenolates



$[Ni(AA)_2]_3$

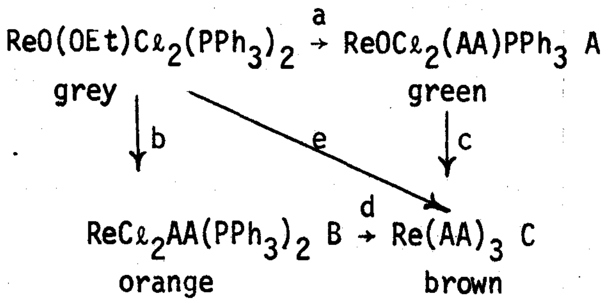
$[Co(AA)_2]_4$

$[Pt(AA)_2(CH_3)_3]_2$

FIGURE: 2

bistriphenylphosphinerhenium(V), $ReO(OEt)C\ell_2(PPh_3)_2$, with β-ketoenols (4,13). A summary of the rhenium β-ketoenolate complexes that were known at the beginning of this work is given in TABLE 1.

The reaction of one β-ketoenol, acetylacetone, with $ReO(OEt)C\ell_2(PPh_3)_2$ in benzene solution, has been described in terms of the following scheme (13).



Reactions a, b and c were described as rapid. The rapid decomposition of A to C was cited as the reason for difficulty in isolating large quantities of product A. Reaction d was considered to be slower proceeding via intermediates such as $ReC\ell(AA)_2PPh_3$ (4). If the reaction was carried out in neat acetylacetone instead of benzene solution, a different product "$Re_2C\ell_2(AA)_4$" was obtained (4). These reactions could be duplicated using oxotrichlorobistriphenylphosphinerhenium(V), $ReOC\ell_3(PPh_3)_2$, as the rhenium-containing starting material. The trans form of this compound, $ReOC\ell_3(PPh_3)_2$, is well established (15, 16).

Recently, detailed structural determinations were made of three of the compounds mentioned above (17). The gross structural features of $ReOC\ell_2(AA)PPh_3$, $ReC\ell_2AA(PPh_3)_2$ and $ReC\ell_2(AA)_2$ are depicted in FIGURES 3, 4 and 5 respectively. The chemically significant features of these structures will be discussed later.

TABLE 1

Rhenium β-ketoenolate Complexes

Re III	Re IV	Re V
$Re(AA)_3$*	$ReC\ell_2(AA)_2$+	$ReOC\ell_2(AA)PPh_3$
$ReC\ell_2(AA)(PPh_3)_2$*		$ReOBr_2(AA)PPh_3$
$ReC\ell_2(HFAA)(PPh_3)_2$*		$ReOI_2(AA)PPh_3$
$ReC\ell_2(TFAA)(PPh_3)_2$*		$ReOC\ell_2(AA)PEt_2Ph$
$ReC\ell_2(TTFA)(PPh_3)_2$*		
$ReBr_2(AA)(PPh_3)_2$		
$ReI_2(AA)(PPh_3)_2$		
$ReC\ell_2(AA)(PEt_2Ph)_2$		
$ReC\ell(AA)_2PPh_3$		
$[ReC\ell_2(AA)]_3$‡		

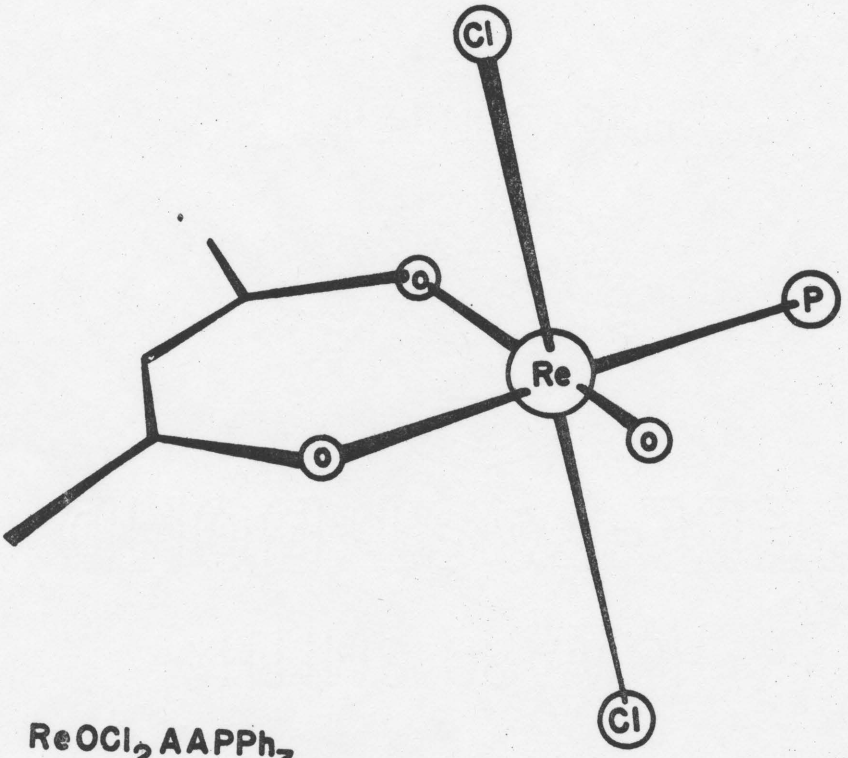
* for abbreviations see Appendix.

\+ originally reported as $Re_2C\ell_4(AA)_4$ (4), but shown to be monomeric in the solid state (10).

‡ reference 14.

FIGURE 3

The structure of $ReOC\ell_2AAPPh_3$

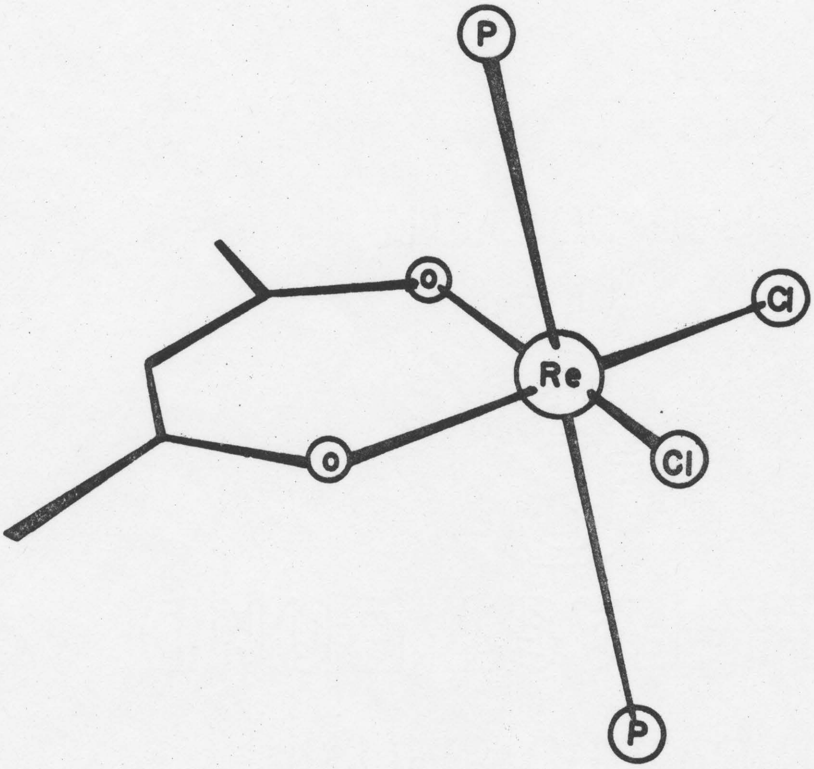


$ReOCl_2AAPPh_3$

FIGURE: 3

FIGURE 4

The structure of $ReC\ell_2AA(PPh_3)_2$

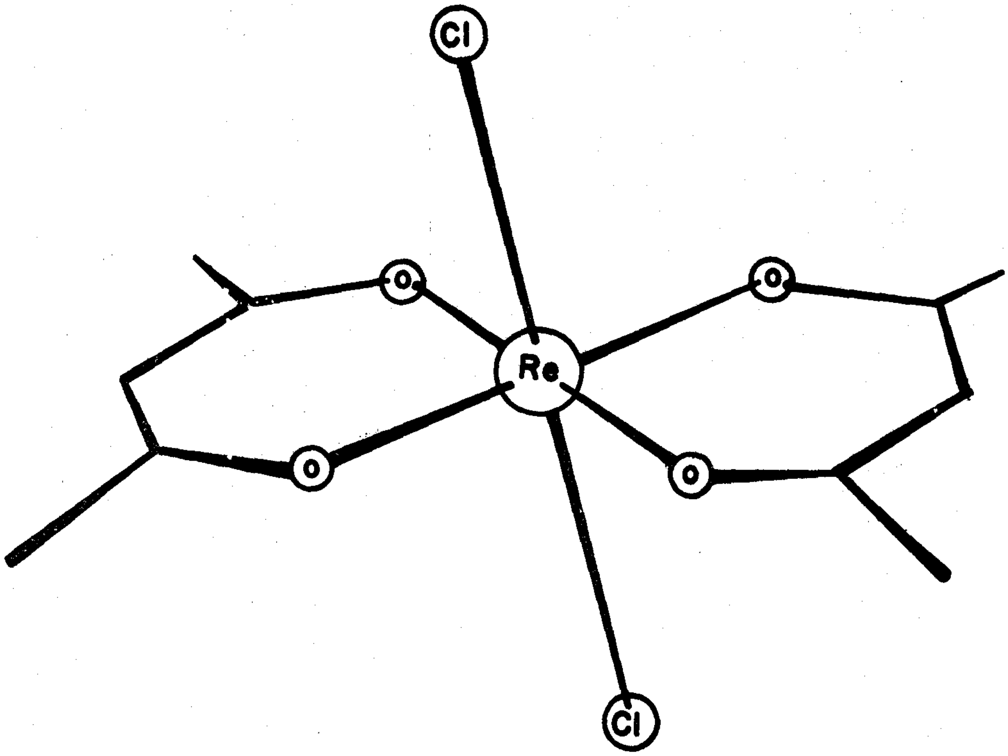


$ReCl_2AA(PPh_3)_2$

FIGURE: 4

FIGURE 5

The structure of $ReC\ell_2(AA)_2$



$ReCl_2(AA)_2$

FIGURE: 5

At present, other workers in this laboratory are performing structural analyses of $Re(HFAA)_3$ (18) and $Re_2(DBM)_2(CO)_6$ (19).

Very recently, a report appeared of some hydrido β-ketoenolate complexes of rhenium (20). The species claimed are listed in TABLE 2. No further comment on this work will be made here.

TABLE 2

Hydrido β-ketoenolate Complexes of Rhenium

Re(III)	Re(IV)	Re(I)
$ReH_2AA(PPh_3)_3$	$ReHAAX_2(PPh_3)_2$ X=I,Br,Cℓ	$ReAACS_2(PPh_3)_2$
$ReHAAX(PPh_3)_3$ X=I,Br,Cℓ		$ReAA(CO)_2(PPh_3)_2$

The aim of this work is to characterize the products of the reaction between $ReO(OMe)C\ell_2(PPh_3)_2$ and β-diketones and to relate them in terms of a reaction scheme. It is rather odd that the products in order of increasing reaction time should be compounds of Re(V), Re(III), Re(IV) followed by a Re(III) compound. Moreover with some structure information now available (17) it should be possible to explain the reactions in this system.

CHAPTER 2

RHENIUM(V) COMPOUNDS

1. Oxo Complexes

In the reaction between $ReO(OMe)C\ell_2(PPh_3)_2$ and acetylacetone, a bright emerald green colour develops initially. The compound responsible for this colour has been identified (4) as oxodichloropentane-2,4-dionatotriphenylphosphinerhenium(V), $ReOC\ell_2AAPPh_3$. Moreover, the crystal structure of the compound produced from the grey isomer of $ReO(OMe)C\ell_2(PPh_3)_2$ or trans-$ReOC\ell_3(PPh_3)_2$ has been determined (17).

The compound is diamagnetic although the rhenium(V) electronic configuration is d^2. Accordingly, some deviation from octahedral symmetry would be expected so that the degeneracy of the t_{2g} set of orbitals is removed, allowing the two electrons to pair spins. In fact, one of the Re-O bond lengths in the chelated β-diketonate anion is significantly longer than the other (17). Furthermore, the distance between the triphenylphosphine phosphorus and the double-bonded oxygen is less than the sum of the respective van der Waal radii (17). The geometry about the rhenium atom does then, deviate significantly from octahedral in the solid state.

The compound $ReOC\ell_2AAPPh_3$ has four possible isomeric forms; these are depicted in FIGURE 6. In addition, isomers I and IV should be optically active. The structure that was determined (17) was that of isomer II.

It was noticed (17) that methylene chloride could be trapped in the lattice of isomer II to the extent of about 10%. In an effort to determine the nature of this phenomenon, two more isomers of the compound were isolated. They could be distinguished visibly from isomer II,which is emerald green, by their colours lime green and blue. The blue isomer seems to trap methylene chloride in the lattice as well. This conclusion is not based on crystallographic evidence as with isomer II (17) but rather on the observation of high carbon and chlorine content in a sample of single crystals. Powdering and vacuum drying of the sample resulted in lower figures for the carbon and chlorine analyses.

A fourth isomer, dark green, of the compound was isolated on one occasion when a mixture of the other three isomers was refluxed in benzene with a little acetylacetone. Only a small amount of the compound was obtained and the preparation could not be duplicated.

The colour differences between the compounds are the result of very subtle changes in position and intensity of an absorption in the near infrared region of the visible spectrum. The electronic spectra of the compounds in the visible and ultraviolet regions are almost identical as seen in TABLE 3.

Compound A appears lime green, compound B is emerald green and is isomer II of FIGURE 6, compound C is blue and compound D is dark green.

It was hoped that characterization using infrared spectroscopy and mass spectrometry would afford a means of determining the stereochemistry of A, C and D. The stretching frequency of the Re=O system might vary with the group trans to it and compounds with cis phosphorus and double-bonded oxygen systems might be expected to give Ph_3PO^+ fragments quite readily in the mass spectrometer.

TABLE 3

Electronic Spectra of $ReOC\ell_2AAPPh_3$ Isomers

Isomer A	Isomer B	Isomer C	Isomer D
38,750 cm^{-1}[*]	38,150	37,900	38,000
3.9×10^3 ε_{max}[+]	5.6×10^3	5.1×10^3	5.6×10^3
36,350	37,200	37,000	37,200
3.4×10^3	5.7×10^3	5.2×10^3	5.7×10^3
34,950	36,200	36,100	36,250
2.4×10^3	5.5×10^3	4.9×10^3	5.6×10^3
29,850	30,400	30,400	30,400
2.0×10^3	3.6×10^3	3.6×10^3	4.0×10^3
25,300	26,200	26,600	26,200
7.3×10^2	8.9×10^2	8.9×10^2	1.0×10^3
15,150	16,260	16,000	16,400
1.8×10	2.1×10	2.3×10	2.6×10

[*] band position

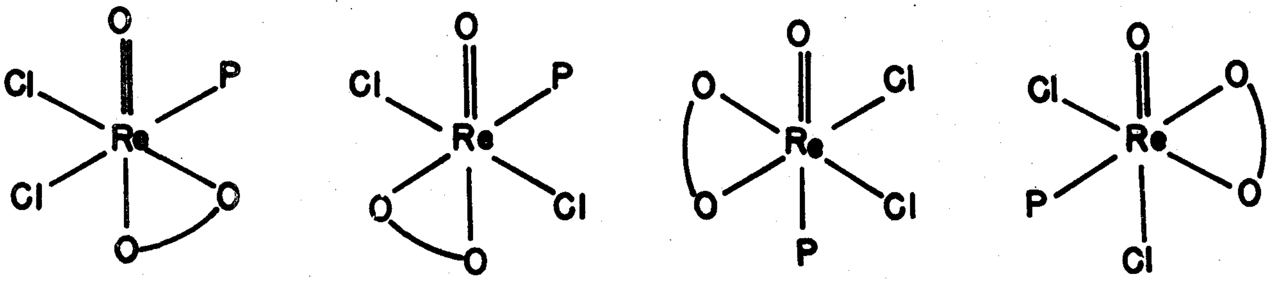
[+] extinction coefficient

FIGURE 6

Isomers of $\mathrm{ReOC\ell_2AAPPh_3}$

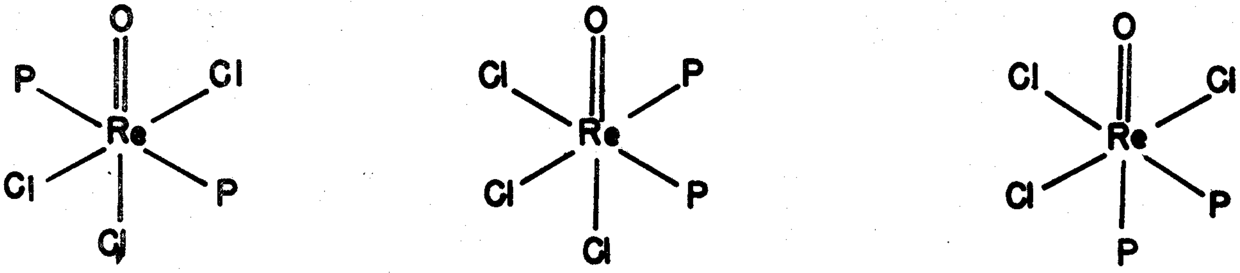
FIGURE 7

Isomers of $\mathrm{ReOC\ell_3(PPh_3)_2}$



I II III IV

FIGURE: 6



E F G

FIGURE: 7

The isomers of $ReO(OMe)C\ell_2(PPh_3)_2$ have not been differentiated with the exception of the grey trans-chloro, trans-triphenylphosphine compound (21). On the other hand, the isomers of $ReOC\ell_3(PPh_3)_2$ have been distinguished (15,22). As shown in FIGURE 7, two have trans Cℓ-Re=O systems and the other has a trans Ph_3P-Re=O system.

The rhenium-oxygen stretching frequencies found for the $ReOC\ell_2AAPPh_3$, $ReOC\ell_3(PPh_3)_2$ and grey $ReO(OMe)C\ell_2(PPh_3)_2$ isomers are given in TABLE 4.

Unfortunately, no simple correlation seems to exist between the Re=O stretching frequency and the nature of the group trans to it. The isomers of $ReOC\ell_2AAPPh_3$ cannot, therefore, be distinguished on the basis of their infrared spectra.

The mass spectral data for the compounds are given in TABLE 5. It was impossible to obtain absolute intensities for the Ph_3P^+ and Ph_3PO^+ fragments. These fragments were several orders of magnitude more abundant than the most abundant rhenium-containing species. The spectra were recorded for two different temperatures in an attempt to ascertain whether the fragmentation pattern was primarily dependent upon the structure of the compound or the conditions of the experiment. The spectrum of compound D was of very low intensity and is not as reliable as the others. The spectrum of compound B run at 300°C showed no peaks at m/e greater than 278 (Ph_3PO^+).

No conclusions as to the structure of A, C and D can be drawn from the mass spectra. However, these data provide the first evidence in this investigation for dimeric species in the rhenium-β-diketone system. The experimental traces show the correct isotope patterns for $Re_2C\ell_4$-containing species. Heretofore the only dimer system reported was $Re_2C\ell_4(AA)_4$ (4)

TABLE 4

Re=0 Stretching Frequencies

Compound	ν Re=0
$ReOC\ell_3(PPh_3)_2$	
E*	969 v.s.
F	982 v.s.
G	981
$ReOC\ell_2AAPPh_3$	
A	970 v.s.
B	978 sh 972 v.s.
C	997 sh 990 v.s.
D	978 v.s.
$ReO(OMe)C\ell_2(PPh_3)_2$	
grey	946 v.s.

---

* letters refer to isomers so designated in FIGURES 6 and 7

TABLE 5

Mass Spectral Data for $ReOC\ell_2AAPPh_3$ Isomers

Fragment	A		B		C		D	
	250°C*	300°C	250°C	300°C	250°C	300°C	250°C	300°C
$Re_2C\ell_4(AA)_2^+$	4**	5	17	-	60	84	-	100
$ReOC\ell_2AAPPh_3^+$	<2	2	12	-	25	36	-	40
$Re_2C\ell_4AA^+$	<2	2	6	-	30	42	-	30
$ReC\ell_2(AA)_2^+$	100	100	10	-	100	100	-	40
$ReOC\ell(AA)_2^+$	<2	6	87	-	13	26	-	90
$ReC\ell(AA)_2^+$	3	12	<2	-	18	24	-	20
$ReO(AA)_2^+$	<2	6	24	-	29	24	-	50
$Re(AA)_2^+$	-	3	<2	-	10	10	-	10
$ReOC\ell_2AA^+$	-	3	100	-	-	<2	-	5
$ReAAC\ell_2^+$	-	<2	13	-	-	<2	-	5
$ReOC\ell AA^+$	75	80	59	-	89	80	-	90
$ReC\ell AA^+$	-	<2	<2	-	-	20	-	30
ReO_2AA^+	-	<2	63	-	<2	20	-	80
$Ph_3P^+:Ph_3PO$***	1:5	1:3	2:1	1:2	1:2	1:2	1:1.5	1:1.5

* refers to temperature of the ionization chamber of the spectrometer

** relative abundance of fragment

***relative abundances not available as these fragments are several orders of magnitude more abundant than Re-containing species which has been shown to be monomeric in the solid state (10).

Attempts to duplicate dimer formation by pyrolysis of these compounds have failed. It may be that the $Re_2C\ell_4(AA)_2^+$ species observed is not a molecular ion but rather a fragmentation or recombination product.

It should be emphasized here that with the exception of compound D, single crystal samples of these compounds have been analysed and they are not mixtures. Moreover, in the case of compound B, the sample, whose mass spectrum appears in TABLE 5, was picked from the same batch of single crystals that provided the crystal studied by X-ray diffraction.

Three isomers of the compound $ReOC\ell_2AAPPh_3$ have been prepared and characterized and a fourth was isolated on one occasion. It has not been possible using ordinary physical techniques to establish the stereochemistry of compounds A, C and D and it is suggested that this problem can only be resolved by crystallographic studies.

2. Nitrido Complexes

The compound nitridochloro-1,1,1-5,5,5-hexafluoropentane-2,4-dionatobistriphenylphosphinerhenium(V), $ReNC\ell HFAA(PPh_3)_2$, has been prepared from sodium hexafluoroacetylacetonate and nitridodichlorobistriphenylphosphinerhenium(V), $ReNC\ell_2(PPh_3)_2$. It is diamagnetic and differs significantly from $ReNC\ell_2(PPh_3)_2$ in that the rhenium is six-coordinate instead of five-coordinate. The structure of $ReNC\ell_2(PPh_3)_2$ has been established (21), - the chlorides and triphenylphosphine groups form a trans, trans square plane about the rhenium and the nitrogen occupies an apical position giving a square pyramid.

The spectrum of $ReNC\ell HFAA(PPh_3)_2$ in the visible and ultraviolet region is given in TABLE 6. Unfortunately the region of the infrared

TABLE 6

Electronic Spectrum of $\mathrm{ReNC\ell HFAA(PPh_3)_2}$

38,150 cm^{-1}

$3.9\mathrm{x}10^3$ ε_{max}

37,050

$3.8\mathrm{x}10^3$

37,600

$3.4\mathrm{x}10^3$

32,050

$3.1\mathrm{x}10^3$

24,800

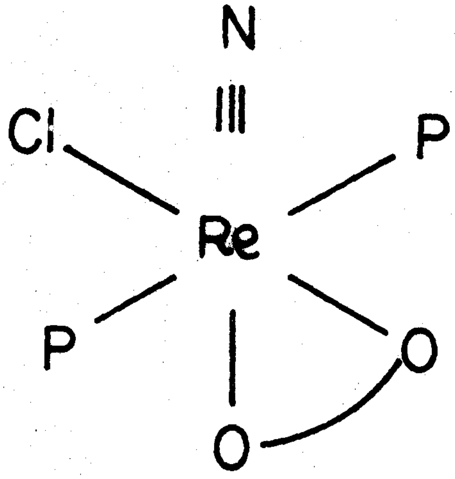
$5.9\mathrm{x}10^2$

19,800

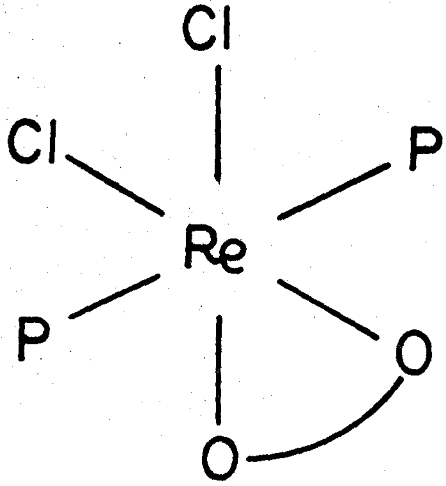
$7.3\mathrm{x}10^2$

FIGURE 8

Possible structures for $ReNC\ell HFAA(PPh_3)_2$ and $ReC\ell_2HFAA(PPh_3)_2$



$ReNClHFAA(PPh_3)_2$



$ReCl_2 \; HFAA(PPh_3)_2$

FIGURE : 8

spectrum where Re≡N stretching vibrations might be expected is masked by the HFAA ligand absorptions.

One oxygen of the HFAA ligand might be expected to bond trans to the Re≡N system and the other could then replace one of the chlorides. This would give a structure similar to that of $ReC\ell_2AA(PPh_3)_2$ as shown in FIGURE 8. X-ray diffraction pattern data for powdered samples of $ReNC\ell HFAA(PPh_3)_2$ and $ReC\ell_2HFAA(PPh_3)_2$ are given in TABLE 7.

The compounds are obviously not isomorphous; there are few if any coincidences between the two patterns. Again it is suggested that structural information be gained by a crystallographic investigation.

This compound, $ReNC\ell HFAA(PPh_3)_2$, is the first nitrido-rhenium complex to be prepared with an oxygen-containing ligand. The other known nitrido-rhenium compounds are, - $[ReO_3N]^{2-}$ (24), $ReNX_2(PPh_3)_2$, $ReNX_2(PR_3)_3$ (25), $K_2[ReN(CN)_4]H_2O$ (26), and $K_3[ReN(CN)_5]$ (27).

It may be that the Re≡N system is more characteristic of rhenium chemistry than heretofore considered. Indeed there may even be as extensive a chemistry of the Re≡N system as there is of the vanadyl system.

TABLE 7

X-ray Diffraction Pattern Data for Powdered Samples of

$ReC\ell_2HFAA(PPh_3)_2$ and $ReNC\ell HFAA(PPh_3)_2$

$ReC\ell_2HFAA(PPh_3)_2$		$ReNC\ell HFAA(PPh_3)_2$	
d	I	d	I
12.470	90	9.686	100
10.589	100	8.775	95
8.441	100	7.375	90
7.762	95	6.810	55
6.394	70	5.776	55
6.046	70	5.025	70
5.461	70	4.575	70
4.809	55	4.191	90
4.411	80	3.912	80
3.934	70	3.655	45
3.757	70	3.500	35
3.473	55	3.255	50
3.363	100	3.107	40
3.148	70	2.782	50
2.914	80	2.661	40
2.818	20	2.571	45
2.710	45	2.503	70
2.614	95	2.277	35
2.543	40	2.152	30
2.428	70	2.085	45
2.321	30	1.987	30
2.246	80		
2.137	60		
2.048	40		
1.986	50		

CHAPTER 3

RHENIUM(IV) COMPOUNDS

Two previous reports of a compound with the stoichiometry $ReC\ell_2(AA)_2$ have described it as a dimer, $Re_2C\ell_4(AA)_4$ (4,16). The compound has been shown (10,17) to be monomeric in the solid state.

In the course of this investigation of the physical properties of $ReC\ell_2(AA)_2$ and its bromide and iodide analogues, no evidence was found for the formation of dimers of the type $Re_2C\ell_4(AA)_4$. In Chapter 2, however, the fragment $Re_2C\ell_4(AA)_2^+$, found in the mass spectrum of $ReOC\ell_2AAPPh_3$, was described.

The structure of $ReC\ell_2(AA)_2$ is given in FIGURE 5 of Chapter 1. In addition to the trans form depicted, the cis compound has been isolated. It was obtained in very low yield from the filtrate residues of several trans-$ReC\ell_2(AA)_2$ preparations. It is more soluble than the trans form as would be expected for a molecule with a dipole moment (28).

The general physical characteristics of the $ReX_2(dik)_2$ compounds studied are given in TABLE 8.

The compounds were characterized by means of their infrared and ultraviolet-visible spectra, mass spectra and magnetic susceptibilities. In addition, X-ray diffraction patterns were obtained for powdered samples of the compounds.

TABLE 9 gives the vibrational spectral data for the $ReX_2(AA)_2$ series. In the case of trans-$ReC\ell_2(AA)_2$, a laser Raman spectrum was obtained but the other compounds were decomposed by the laser so such data is not

TABLE 8

Physical Characteristics of $ReX_2(dik)_2$* Compounds

Compound	Colour	Melting Point**	μ_{eff} at 293°K
trans-$ReC\ell_2(AA)_2$	orange	~275°C	2.83 B.M.
cis-$ReC\ell_2(AA)_2$	reddish-brown	~255°C	not known
$ReBr_2(AA)_2$	reddish-orange	~265°C	2.79 B.M.
$ReI_2(AA)_2$	dark red	>325°C	2.61 B.M.
$ReC\ell_2(DBM)_2$*	dark red	>325°C	3.22 B.M.

* See Appendix for abbreviations

** Actually decomposition temperature

available. Because of their limited solubilities in suitable solvents, the compounds could not be investigated in solution.

Assignments of infrared bands in TABLE 9 are based on comparisons with the spectra of the titanium, zirconium and hafnium compounds of this type (29,30). The Re-halogen bands were assigned by comparing the spectra of $ReC\ell_2(AA)_2$, $ReBr_2(AA)_2$ and $ReI_2(AA)_2$, for example, the band at 309 cm^{-1} present in the spectrum of $ReC\ell_2(AA)_2$ and absent from the spectra of $ReBr_2(AA)_2$ and $ReI_2(AA)_2$ was assigned ν(Re-Cℓ).

It is seen that the spectra of cis and trans $ReC\ell_2(AA)_2$ are nearly identical. Furthermore, the ν(Re-O) and ν(Re-Cℓ) bands of trans-$ReC\ell_2(AA)_2$ appear in both the infrared and Raman spectra. Such a coincidence of bands was used as evidence for a cis configuration of the titanium, zirconium and hafnium compounds (29,30). The trans compound has a centre of symmetry and the infrared-active modes should be Raman inactive. The structure of trans-$ReC\ell_2(AA)_2$ is known (17) and there are as many coincidences between the infrared and Raman spectra as observed for the titanium, zirconium and hafnium compounds. The evidence given in support of a cis configuration for these compounds cannot be considered compelling.

Dipole moment measurements have confirmed a cis configuration for these compounds in solution (31). Recently trans-$GeC\ell_2(AA)_2$ and trans-$TiI_2(AA)_2$ have been described (32,33) and it is suggested that as with the rhenium compounds both cis and trans forms exist. Unfortunately the low solubility of trans-$ReC\ell_2(AA)_2$ and the limited quantity of cis-$ReC\ell_2(AA)_2$ available preclude dipole moment or proton magnetic resonance investigations for direct comparison with the titanium, zirconium and hafnium system.

The identity of trans-$ReC\ell_2(AA)_2$ has been confirmed by a structural determination (10,17). Mass spectra, analyses and X-ray diffraction patterns

TABLE 9

Vibrational Spectral Data for $ReX_2(AA)_2$ Compounds

cis-$ReC\ell_2(AA)_2$	trans-$ReC\ell_2(AA)_2$		$ReBr_2(AA)_2$	$ReI_2(AA)_2$	Assignment
I.R.	I.R.	Raman	I.R.	I.R.	
	1620w		1630w	1630w	
1540sh	1535v.s.		1540v.s.	1535v.s.	$\nu_s(C\cdots O)$
1515v.s.	1480sh.		1490sh.	1490sh.	
1450m.	1440sh.		1440sh.		
1405w.	1420s.		1430s.	1420s.	$\nu_{as}(C\cdots C)$
1380m.	1385sh.		1390sh.	1380s.	$\delta_d(CH_3)$
1360m.	1375s.	1368m.	1380s.	1360s.	$\delta_s(CH_3)$
1320s.	1318s.		1320s.	1319s.	$\nu_{as}(C\cdots O)$
	1296sh.	1299s.	1295sh.	1293sh.	
1285s.	1287s.		1287s.	1285s.	$\nu_s(C\cdots C)$
	1193w.	1204w.	1191w.	1190v.w.	$\delta(C-H)$
	1189sh.		1188sh.		
1027s.	1031s.	1025w.	1031s.	1029s.	$\rho(CH_3)$
1015sh.	1021sh.		1020sh.	1021sh.	
938s.	938s.	948m.	937s.	935s.	$\nu(C-CH_3)$
906w.					
808s.	812s.		810s.	804s.	
	760v.w.		755v.w.		
	744w.		747sh.		
			742w.		
720v.w.	720v.w.		720v.w.	720v.w.	
	698sh.	694m.	697sh.		
684s.	686s.		685s.	681s.	$\nu(M-O)+\delta(C-CH_3)$ or $\delta(ring)$
650w.	650w.	653v.w.	646v.w.	644v.w.	
604s.	610s.	607w.	606s.	603s.	$\nu(M-O)+\delta(C-CH_3)$ or $\delta(ring)$
	584v.w.		582v.w.	584v.w.	
		554w.			

TABLE 9 continued

Vibrational Spectral Data for $ReX_2(AA)_2$ Compounds

cis- $ReC\ell_2(AA)_2$	trans-$ReC\ell_2(AA)_2$		$ReBr_2(AA)_2$	$ReI_2(AA)_2$	Assignment
I.R.	I.R.	Raman	I.R.	I.R.	
	526sh.		523sh.		
	520w.		516w.	515v.w.	
	510w.		507w.		
472sh.	501sh.		500sh.		
460s.	464s.	479v.w.	462s.	460s.	ν(Re-O)
		448v.w.			
416v.w.	422m.	422w.	420m.	417m.	
346s.	309v.s.	320w.			ν(Re-Cℓ)
336s.	286sh.	301m.			
259m.	253s.	262v.w.	255s.	251sh.	ν(Re-O)
208m.	245s.	245v.w.	248sh.	245s.	
		221w.			
		207m.	208m.		
			190m.		ν(Re-Br)
				170s.	ν(Re-I)

of powdered samples were examined in order to establish cis-$ReC\ell_2(AA)_2$. In addition, $ReBr_2(AA)_2$ and $ReI_2(AA)_2$ were characterized. On the basis of their solubilities, the samples of $ReBr_2(AA)_2$ and $ReI_2(AA)_2$ investigated are assumed to be trans.

Mass spectral data for both $ReC\ell_2(AA)_2$ isomers are given in TABLE 10. TABLE 11 gives mass spectral data for $ReBr_2(AA)_2$ and $ReI_2(AA)_2$.

The conditions under which all the mass spectra were obtained were, - source temperature 210-220°C, ionizing voltage 70 e.V. and accelerator potential 8 K.V. In all cases, the fragment with the highest m/e value corresponds to $ReX_2(AA)_2^+$, that is, there is no evidence of $Re_2X_4(AA)_4^+$ or fragmentation products attributable to such a species. The major non-rhenium-containing fragments observed were $C_2H_3O^+$(m/e 43) and $C_5H_7O^+$(m/e 83) as well as $C_5H_8O_2^+$(m/e 100).

A comparison of the relative intensities of the $Re(AA)_2^+$ fragment for the $C\ell$, Br and I series suggests that the ease of formation of such a fragment or the ease with which halogen is lost varies in the order $C\ell < Br < I$. This is just the inverse of order of rhenium-halogen bond strengths.

That the two forms of $ReC\ell_2(AA)_2$ are indeed different is confirmed by the data given in TABLE 12. X-ray diffraction patterns of powdered samples of all of the $ReX_2(AA)_2$ compounds were recorded. The data for $ReBr_2(AA)_2$ and $ReI_2(AA)_2$ are given in TABLE 13.

There are several coincidences in the patterns of the two $ReC\ell_2(AA)_2$ isomers but the patterns are sufficiently different that the compounds cannot be said to be isomorphous. It is concluded that they are not isostructural. As there is only one possibility other than trans for a

TABLE 10

Mass Spectral Data for $ReC\ell_2(AA)_2$

Fragment	m/e	Intensity	
		trans	cis
$ReC\ell_2(AA)_2^+$	459 457 455 453	100	100
$ReC\ell(AA)_2^+$	422 420 418	6	4
$ReAA_2^+$	385 383	3	2
$ReC\ell AA(C_3H_4O)^+$	379 377 375	-	4
$ReOC\ell_2AA^+$	376 374 372 370	<2	5
$ReC\ell_2AA^+$	360 358 356 354	<2	2
$ReOC\ell AA^+$	339 337 335	63	62
$ReC\ell AA^+$	323 321 319	<2	5
$ReOAA^+$	302 300	2	2
$ReOC\ell_2^+$	277 275 273 271	5	7

TABLE 11

Mass Spectral Data for $ReBr_2(AA)_2$ and $ReI_2(AA)_2$

	$ReBr_2(AA)_2$		$ReI_2(AA)_2$	
Fragment	m/e	Intensity	m/e	Intensity
$ReX_2(AA)_2^+$	547 545 543 541	100	639 637	86
$ReX(AA)_2^+$	466 464 462	7	512 510	69
$ReX(AA)_2^{2+}$	233 232 231	7	256 255	17
$Re(AA)_2^+$	385 383	74	385 383	100
$ReOX(AA)^+$	383 381 379	30	429 427	10
$ReOH(AA)^+$	303 301	3	303 301	23
$ReO(AA)^+$	302 300	2	302 300	10
$ReOX_2^+$	365 363 361 359	6	457 455	5

TABLE 12

X-ray Diffraction Pattern Data for Powdered Samples of $\mathrm{ReC}\ell_2(\mathrm{AA})_2$ Isomers

trans $\mathrm{ReC}\ell_2(\mathrm{AA})_2$		cis $\mathrm{ReC}\ell_2(\mathrm{AA})_2$	
d	I	d	I
6.921	70	8.370	<5
6.254	80	6.804	100
5.794	75	6.411	90
5.517	80	5.712	90
5.254	80	5.211	15
4.114	10	4.458	10
3.978	65	3.983	80
3.810	55	3.782	10
3.655	70	3.616	10
3.497	75	3.416	75
3.306	100	3.257	<5
3.220	60	3.144	5
3.094	65	3.087	5
2.882	30	2.923	5
2.753	10	2.832	15
2.638	35	2.720	<5
2.535	75	2.620	15
2.473	80	2.569	15
2.404	60	2.520	20
2.335	10	2.327	15
2.271	30	2.276	15
2.247	50	2.244	
2.076	10	2.090	
2.003	25	1.973	
1.940	25	1.932	
1.913	30	1.894	
1.863	20	1.726	
1.826	45	1.703	
1.801	30	1.481	
1.756	25		
1.714	20		
1.654	10		
1.605	30		

TABLE 13

X-ray Diffraction Pattern Data for Powdered Samples of $ReBr_2(AA)_2$ and $ReI_2(AA)_2$

$ReBr_2(AA)_2$		$ReI_2(AA)_2$	
d	I	d	I
10.178	70	7.500	45
7.872	55	6.544	90
7.431	35	6.237	100
7.030	50	5.867	70
6.188	100	3.845	70
5.851	35	3.555	90
5.407	25	3.417	60
4.823	20	3.261	40
4.086	30	2.942	10
3.943	35	2.797	10
3.826	40	2.503	10
3.720	40	1.956	30
3.638	40	1.881	10
3.437	40	1.777	15
3.379	10		
3.162	20		
2.916	4		
2.839	6		
2.746	12		
2.631	25		
2.493	20		
2.444	10		
2.373	5		
2.323	5		
2.263	10		
2.216	5		

TABLE 14

Electronic Spectral Data for $ReX_2(dik)_2$ Compounds

trans-$ReC\ell_2(AA)_2$	cis-$ReC\ell_2(AA)_2$	$ReBr_2(AA)_2$	$ReI_2(AA)_2$	$ReC\ell_2(DBM)_2$
36,230 cm^{-1}	39,050	36,350	34,000	35,450
$4.8x10^3$ ε_{max}	$7.8x10^3$	$5.1x10^3$	$7.2x10^3$	$2.6x10^4$
30,100	30,300	27,800	28,100	29,400
$1.6x10^3$	$3.1x10^3$	$3.2x10^3$	$2.8x10^3$	$8.6x10^3$
23,600	25,000	22,750	24,050	20,750
$8.1x10^2$	$1.6x10^3$	$1.4x10^3$	$4.2x10^3$	$3.0x10^3$
19,900	-	20,000	18,200	19,600
$2.6x10^2$	-	$6.8x10^2$	$2.5x10^3$	$3.1x10^3$

monomeric $ReC\ell_2(AA)_2$ compound, it is concluded that the cis-form has been established.

Another feature which distinguishes the cis and trans forms of $ReC\ell_2(AA)_2$ is the electronic spectrum in the ultraviolet-visible region. Spectral data for the $ReX_2(dik)_2$ compounds are presented in TABLE 14.

It is customary to interpret such data in terms of an energy level diagram and assign the observed bands to specific electronic transitions (34). However, a satisfactory energy level diagram for Re(IV) is not available at this time and therefore, no attempt will be made at assigning particular electronic transitions.

Because experimentally determined values for the spin-orbit coupling constant ζ'_{5d} and the ligand field splitting 10 Dq were lacking, an empirical approach was used to interpret the magnetic susceptibility data for these compounds.

The magnetic susceptibilities of these compounds obey a modified form of the Curie-Weiss law. The equation,

$$\chi = \frac{C}{T+\Theta} + \alpha \qquad (1)$$

has been used by Eisenstein (35) to interpret the magnetic properties of potassium hexachlororhenate. The normal Curie-Weiss equation,

$$\chi = \frac{C}{T+\Theta} \qquad (2)$$

has been modified by the inclusion of a temperature independent parameter α. Equation (1) may be rewritten in the form,

$$\chi - \alpha = \frac{C}{T+\Theta}$$

where α is the contribution to the susceptibility from temperature independent paramagnetism (T.I.P.).

If the temperature independent term is ignored, a "break" occurs in the Curie-Weiss plot of $1/\chi$ vs. T. as shown in FIGURE 9. This break is not the result of a magnetic transition. A Curie-Weiss plot $1/\chi$ vs. T. for the temperature range 5°K to 230°K, FIGURE 10, shows a gentle curvature over the temperature range. This data was obtained using a vibrating magnetometer and the susceptibilities measured in this way are about 10% lower than those obtained with the Gouy apparatus used in this work. The magnetometer measurements are out by at least 3% (36) which leaves a 7% difference unaccounted for. No explanation can be offered for this discrepancy.

The magnetic susceptibility data for the compounds are given in TABLES 15, 16, 17 and 18. It can be seen that the magnetic moment, μ_{eff}, varies somewhat with temperature for the bromide and iodide but hardly at all for the chloride. In the case of the hexahalorhenates, a variation of μ_{eff} with temperature has been interpreted "as reflecting magnetic interactions" (37). Moreover, the relative magnitude of Θ was said to indicate the amounts of antiferromagnetic interaction in these compounds (37).

A detailed study has been made of the magnetic susceptibility of potassium hexachlororhenate (IV) and potassium hexabromorhenate (IV) (38). The Curie points have been determined as 12.4±0.5° and 15.3±0.5°K for $K_2ReC\ell_6$ and K_2ReBr_6 respectively. The equation,

FIGURE 9

Plot of $1/\chi$ versus T for trans-$ReC\ell_2(AA)_2$ (Gouy data)

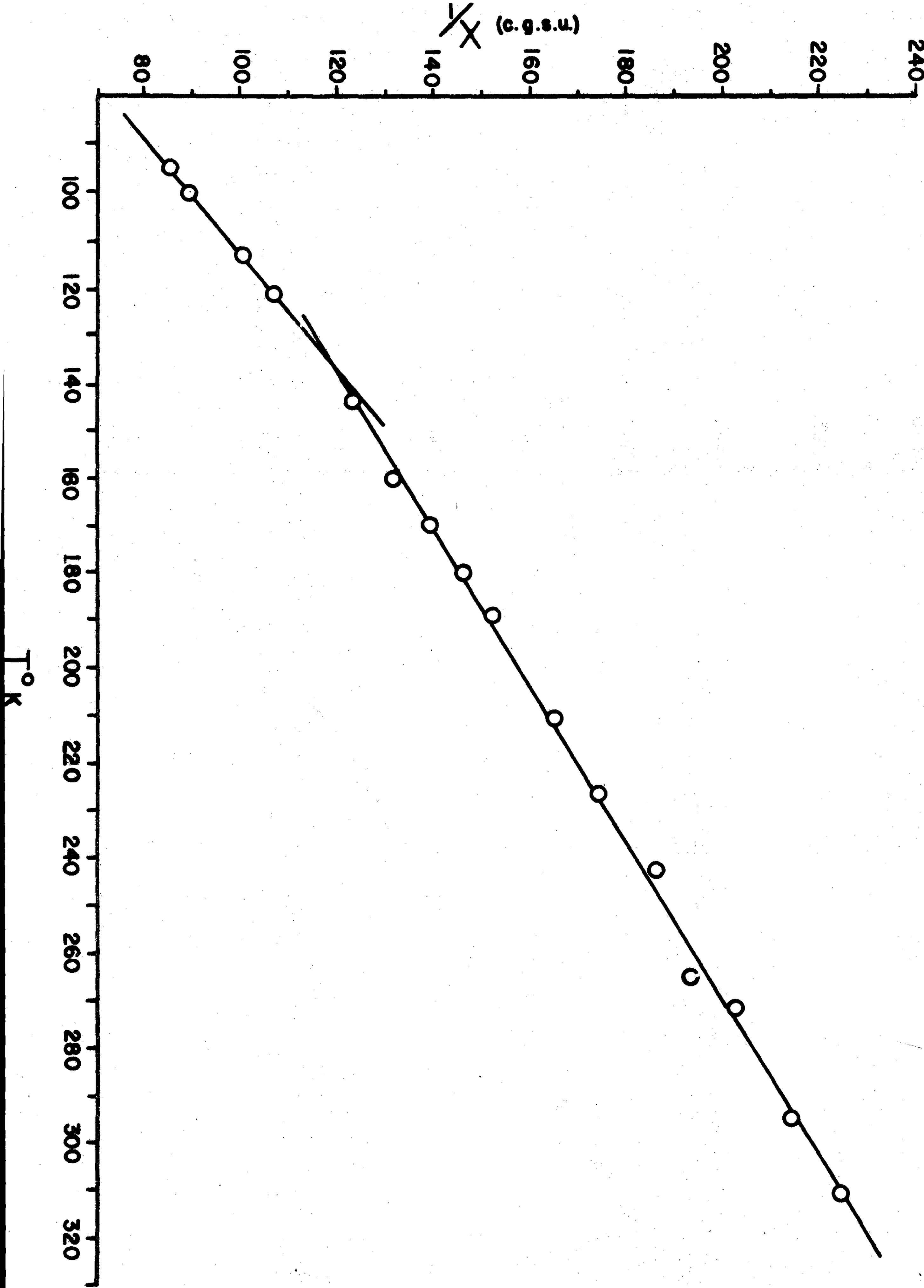

1/χ (c.g.s.u.)
80
100
120
140
160
180
200
220
240
T°K
100
120
140
160
180
200
220
240
260
280
300
320

FIGURE 10

Plot of 1/χ versus T for trans-$ReC\ell_2(AA)_2$

(Magnetometer data)

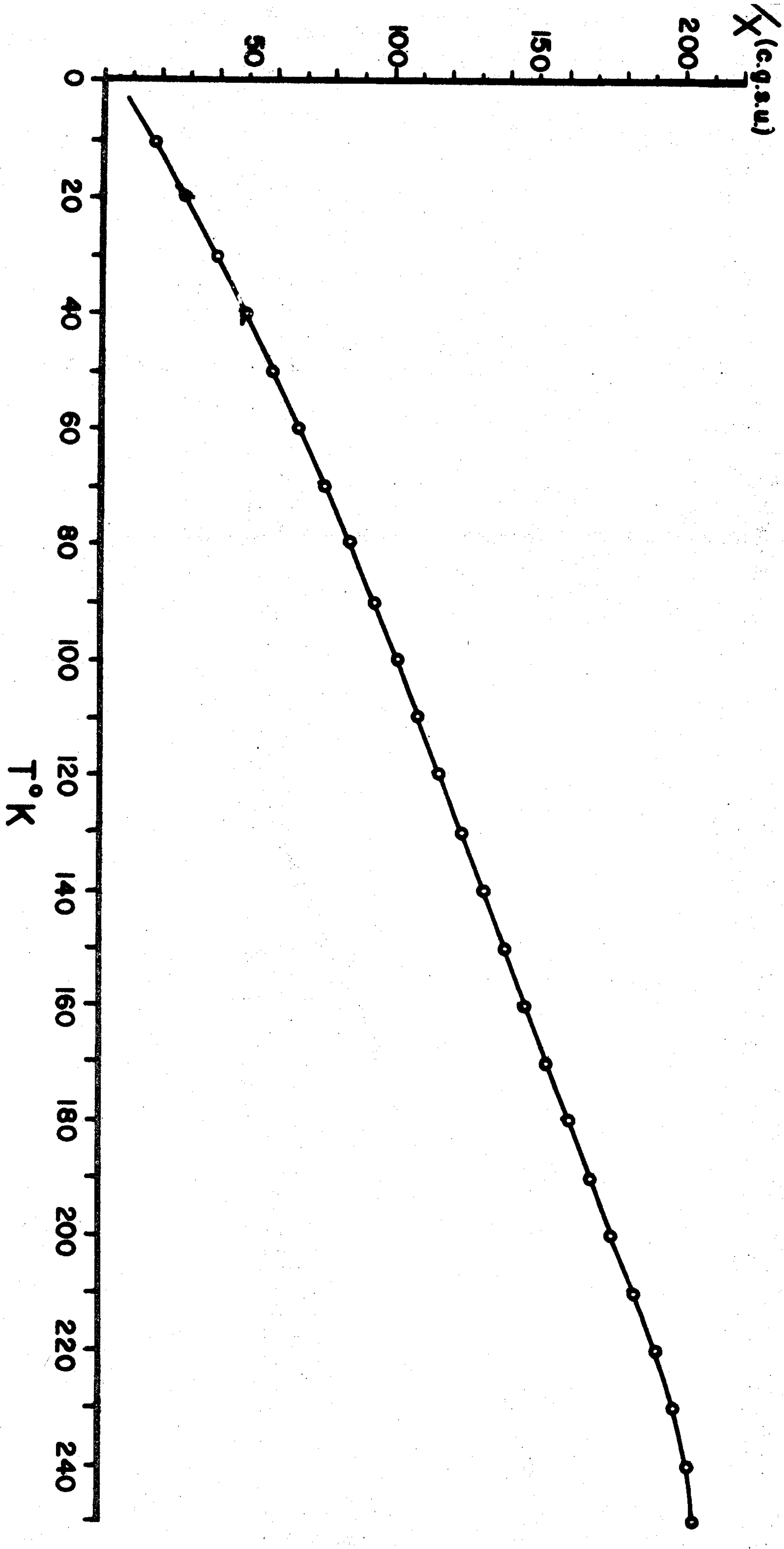

1/χ (c.g.s.u.)
200
150
100
50
0
20
40
60
80
100
120
140
160
180
200
220
240
T°K

TABLE 15

Magnetic Data for trans-$\text{ReC}\ell_2(\text{AA})_2$

$$\chi_{obs} - 1315 = \frac{1.003}{T+2}$$

T°K	a $(\chi_{obs}-1315)$ cgsu.	b $\frac{1.003}{T+2}$ cgsu.	%diff. (a-b)	μ_{eff}
95	.010421	.010340	+.8	2.81
100	.009839	.009833	+.1	2.82
113	.008656	.008722	-.8	2.82
121	.008036	.008154	-1.5	2.82
144	.006816	.006870	-.8	2.82
160	.006319	.006191	+2.1	2.83
170	.005859	.005831	+.5	2.83
180	.005511	.005539	+.5	2.84
189	.005251	.005277	+.5	2.84
210	.004731	.004751	+.4	2.84
226	.004399	.004422	+.5	2.84
242	.004111	.004056	-1.4	2.81
265	.003757	.003859	+2.7	2.87
271	.003674	.003625	-1.4	2.81
294	.003389	.003352	-1.1	2.82
310	.003215	.003146	-2.2	2.80
			Av.	2.83

Errors in the measurement of temperature and weighing errors contribute a 1% uncertainty in χ at low temperatures and .5% at higher temperatures.

TABLE 16

Magnetic Data for $ReBr_2(AA)_2$

$$\chi_{obs} - 1295 = \frac{1.004}{T+12}$$

T°K	a $(\chi_{obs}-1295)$cgsu	b $\frac{1.004}{T+12}$cgsu	%diff (a-b)	μ_{eff}
85	.010391	.010351	+.4	2.66
93	.009494	.009562	-.7	2.68
111	.008135	.008163	-.3	2.70
125	.007271	.007328	-.8	2.72
145	.006361	.006395	-.5	2.73
159	.005853	.005871	-.3	2.74
177	.005451	.005312	+2.6	2.75
191	.005003	.004946	+1.2	2.76
206	.004666	.004606	+1.3	2.77
222	.004303	.004291	+.3	2.77
238	.004040	.004016	+.6	2.78
255	.003749	.003760	-.3	2.78
268	.003552	.003586	-1.0	2.78
286	.003288	.003369	-2.5	2.79

Errors in measurements are as mentioned in TABLE 3.

TABLE 17

Magnetic Data for $ReI_2(AA)_2$

$$\chi_{obs} - 1380 = \frac{1.005}{T+55}$$

T°K	a $(\chi_{obs}-1380)$ cgsu	b $\frac{1.005}{T+55}$ cgsu	%diff (a-b)	μ_{eff}
82	.007442	.007336	+1.4	2.20
96	.006715	.006656	+.9	2.27
103	.006367	.006361	+.1	2.30
113	.005926	.005982	-.9	2.33
124	.005507	.005615	-2.0	2.37
135	.005271	.005289	-.3	2.40
144	.004964	.005050	-1.7	2.42
159	.004687	.004696	-.2	2.45
174	.004380	.004389	-.2	2.48
190	.004114	.004102	+.3	2.51
205	.003858	.003865	-.2	2.53
221	.003633	.003641	-.2	2.55
238	.003457	.003430	+.8	2.57
255	.003275	.003242	+1.0	2.58
269	.003152	.003102	+1.6	2.59
286	.002967	.002947	+.8	2.61

TABLE 18

Magnetic Data for $ReC\ell_2(DBM)_2$

$$\chi_{obs} - 2100 = \frac{1.660}{T+85}$$

T°K	a $(\chi_{obs}-2100)$cgsu	$\frac{1.660}{T+85}$cgsu	%diff (a-b)	μ_{eff}
86	9701	9708	-.1	2.59
96	9171	9196	+.3	2.66
108	8601	8585	-.2	2.73
124	7943	7912	-.4	2.81
139	7411	7301	-1.5	2.86
153	6975	6873	-1.5	2.91
171	6484	6526	+.6	3.00
185	6148	6149	-	3.03
202	5784	5792	+.1	3.07
215	5533	5507	-.5	3.09
231	5253	5232	-.4	3.12
247	5000	5028	+.6	3.16
260	4812	4865	+1.1	3.19
276	4598	4671	+1.6	3.22

$$\chi_M = \frac{\mu_{S.O.}{}^2 \beta_M{}^2 [1-(4\zeta'_{5d}/30\ Dq)]^2}{T+\Theta} + \chi_D + \chi_h{}^* \qquad (3)$$

was used to fit the data. This treatment gave values for Θ and the Curie constant of 55° and 1.633 for K_2ReCl_6 and 76° and 1.548 for K_2ReBr_6. The temperature independent term χ_h was estimated using Griffith's (39) expression,

$$\chi_h = 8N\beta_M{}^2/10Dq^{\dagger} \qquad (4)$$

This gives $\chi_h = 65 \times 10^{-6}$ cm and $\chi_h = 75 \times 10^{-6}$ cgsu for the chloride and bromide complex respectively.

In TABLE 19 the values of Θ and χ_h for the $ReX_2(AA)_2$ series are contrasted with those for K_2ReX_6.

The temperature independent contribution to the susceptibility of the $ReX_2(AA)_2$ compounds was determined empirically. The data was fitted to Equation (1) and the values given are those which gave the best fit.

The value of Θ is sometimes taken as a measure of the Heisenberg exchange interaction between magnetic atoms or ions (39). In K_2ReCl_6 and K_2ReBr_6 this interaction is of the antiferromagnetic type and occurs by superexchange via the halogen atoms (38). Superexchange is increased as the electronegativity of the anion decreases (40).

---

* $\mu_{S.O.}$ is the effective spin-only moment, 3.87 in this case
B.M. is the Bohr magneton
χ_D is the diamagnetic contribution of all the atoms in the molecule
χ_h is the Van Vleck temperature independent paramagnetism
ζ_{5d} is the one-electron spin-orbit coupling constant in the solid state

† N is Avogadro's Number
10 Dq = 31,500 and 27,000 cm^{-1} for chloride and bromide respectively (18)

TABLE 19

Θ and T.I.P. Values for some Re(IV) Compounds

Compound	Θ	χ_h(T.I.P.)
trans-$ReC\ell_2(AA)_2$	2	1315
$K_2ReC\ell_6$	55	65
$ReBr_2(AA)_2$	12	1295
K_2ReBr_6	76	75
$ReI_2(AA)_2$	55	1380
K_2ReI_6	∿100	--

There seems to be little antiferromagnetic interaction between rhenium ions in trans-$ReC\ell_2(AA)_2$. The amount of antiferromagnetic interaction, reflected by the magnitude of Θ, increases in the order $C\ell < Br < I$ as expected. (This is the order of decreasing electronegativity.)

In $K_2ReC\ell_6$ and K_2ReBr_6 superexchange may occur along all three of the crystal axes. In trans-$ReC\ell_2(AA)_2$, such an interaction could only take place along one axis. The amount of antiferromagnetic interaction occurring via superexchange should, therefore, be less for $ReX_2(AA)_2$-type compounds than for $K_2ReC\ell_6$ or K_2ReBr_6. Quantitative comparisons cannot be made, however, because the crystal structures of the two types of compounds are different; $ReC\ell_2(AA)_2$ is triclinic and $K_2ReC\ell_6$ is face-centered cubic. The Θ values for the $ReX_2(AA)_2$ compounds are, as expected, less than those for the K_2ReX_6 compounds.

Temperature independent paramagnetism in these compounds arises from the second order Zeeman effect. That is, the ground state is modified by 'mixing in' an amount of some higher state proportional to the field. If the higher state mixed in is much more than kT above the ground state, no thermal distribution between the levels can occur and the susceptibility from this effect is temperature independent. In $K_2ReC\ell_6$, this 'higher level' mixed in is about 31,500 cm^{-1} (38) above the ground level and the temperature independent contribution to the susceptibility is somewhat less than 100×10^{-6} cgsu as expected for such a situation. In the $ReX_2(AA)_2$ compounds, however, the temperature independent contribution to the susceptibility is much greater. In this case, splitting of the electronic energy levels occurs by both spin orbit coupling and a descent in symmetry to D_{4h} (with respect to O_h for $K_2ReC\ell_6$). If these effects combine to reduce the energy separation between the ground level and that level which is mixed in under the second order Zeeman effect then a temperature independent paramagnetism which exceeds 1000×10^{-6} cgsu (39) is possible. Thus, temperature independent paramagnetism in the $ReX_2(AA)_2$ compounds would be expected to be considerably larger than that observed for $K_2ReC\ell_6$ or K_2ReBr_6.

CHAPTER 4

RHENIUM(III) COMPOUNDS

1. Dihalodiketonatobistriphenylphosphinerhenium(III)Complexes

The most characteristic feature of the reaction between β-diketones and $ReO(OMe)C\ell_2(PPh_3)_2$ (or $ReOC\ell_3(PPh_3)_2$) is the formation of rhenium(III) complexes of the type $ReC\ell_2dik(PPh_3)_2$. Some of the β-diketones used in this work did not give Re(V) or Re(IV) complexes but all gave Re(III) complexes.

Chloride, bromide and iodide analogues of $ReX_2dik(PPh_3)_2$ have been prepared for eight different β-diketone ligands. The series of compounds is summarized in TABLE 20.

In order to ascertain whether or not all the compounds prepared were members of this series, they were characterized by means of their electronic spectra in the ultraviolet and visible region and by magnetic susceptibility measurements.

The spectral data given in the rather extensive TABLE 21 show no really coherent trends that might be correlated with a change in β-diketone or in halide ion. The gross features of these spectra are, in fact, similar to the spectra of the $ReX_2(AA)_2$ compounds given in Chapter 3. This lends credibility to the suggestion that the bands observed are the result of charge transfer processes involving, primarily, the π system of the β-diketonate chelate ring.

Magnetic susceptibility data for some of the compounds are plotted in FIGURES 11-17. Data for some of the compounds listed in TABLE 20

TABLE 20

Compounds of the type $ReX_2dik(PPh_3)_2$

dik	X = Cℓ	X = Br	X = I
AA	✓	✓	✓
DBM	✓	✓	✓
HFAA*	✓	✓	✓
BA	✓	✓	✓
TFBA	✓	✓	✓
TFTA	✓	✓	✓
EAA	✓	✓	✓
EBA	✓	✓	✓

* see Appendix for abbreviations

TABLE 21

Electronic Spectra of $ReX_2dik(PPh_3)_2$ Compounds

$ReC\ell_2AA(PPh_3)_2$	$ReBr_2AA(PPh_3)_2$	$ReI_2AA(PPh_3)_2$
39,000 cm^{-1}	39,000	37,500
$1.1\mathrm{x}10^{4}$ ε_{max}	$1.3\mathrm{x}10^{4}$	$1.3\mathrm{x}10^{4}$
33,800	33,300	33,300
$3.9\mathrm{x}10^{3}$	$2.5\mathrm{x}10^{3}$	$4.0\mathrm{x}10^{3}$
29,000	29,000	26,700
$2.6\mathrm{x}10^{3}$	$3.2\mathrm{x}10^{3}$	$4.1\mathrm{x}10^{3}$
23,600	23,000	22,100
$1.9\mathrm{x}10^{3}$	$2.4\mathrm{x}10^{3}$	$4.8\mathrm{x}10^{3}$
20,400	20,000	19,200
$6.2\mathrm{x}10^{2}$	$4.4\mathrm{x}10^{2}$	$1.7\mathrm{x}10^{3}$

$ReC\ell_2BA(PPh_3)_2$	$ReBr_2BA(PPh_3)_2$	$ReI_2BA(PPh_3)_2$
39,200	38,500	36,500
$1.7\mathrm{x}10^{4}$	$1.6\mathrm{x}10^{4}$	$1.1\mathrm{x}10^{4}$
35,100	34,700	31,700
$7.9\mathrm{x}10^{3}$	$8.3\mathrm{x}10^{3}$	$5.7\mathrm{x}10^{3}$
31,600	30,800	29,100
$5.5\mathrm{x}10^{3}$	$6.4\mathrm{x}10^{3}$	$3.6\mathrm{x}10^{3}$
26,000	25,300	26,600
$2.0\mathrm{x}10^{3}$	$2.1\mathrm{x}10^{3}$	$2.5\mathrm{x}10^{3}$
23,300	22,200	21,700
$3.6\mathrm{x}10^{3}$	$3.3\mathrm{x}10^{3}$	$3.7\mathrm{x}10^{3}$
18,200	18,000	19,500
$1.8\mathrm{x}10^{3}$	$1.7\mathrm{x}10^{3}$	$2.9\mathrm{x}10^{3}$
		17,700
		$1.5\mathrm{x}10^{3}$

TABLE 21 continued

$\mathrm{ReC\ell_2DBM(PPh_3)_2}$	$\mathrm{ReBr_2DBM(PPh_3)_2}$	$\mathrm{ReI_2DBM(PPh_3)_2}$
39,200	38,500	36,600
2.0×10^4	1.8×10^4	1.1×10^4
31,700	31,500	31,200
1.1×10^4	1.1×10^4	1.0×10^4
29,400	29,400	27,500
1.1×10^4	9.9×10^3	6.4×10^3
22,200	21,900	21,400
4.3×10^3	4.6×10^3	4.1×10^3
17,400	17,400	19,100
3.5×10^3	2.3×10^3	3.4×10^3
16,400	16,500	16,300
2.7×10^3	2.4×10^3	2.3×10^3

$\mathrm{ReC\ell_2EAA(PPh_3)_2}$	$\mathrm{ReBr_2EAA(PPh_3)_2}$	$\mathrm{ReI_2EAA(PPh_3)_2}$
39,400	38,600	37,600
1.3×10^4	1.2×10^4	7.9×10^3
29,900	29,600	31,800
2.2×10^3	3.0×10^3	2.5×10^3
25,100	24,600	27,900
1.8×10^3	2.1×10^3	2.4×10^3
22,500	21,400	22,600
1.1×10^3	1.4×10^3	2.0×10^3
		19,400
		1.1×10^3

$\mathrm{ReC\ell_2EBA(PPh_3)_2}$	$\mathrm{ReBr_2EBA(PPh_3)_2}$	$\mathrm{ReI_2EBA(PPh_3)_2}$
39,200	38,500	36,600
1.6×10^4	1.5×10^4	1.3×10^4
33,900	32,900	32,800
8.0×10^3	8.1×10^3	7.2×10^3

TABLE 21 continued

$ReC\ell_2EBA(PPh_3)_2$	$ReBr_2EBA(PPh_3)_2$	$ReI_2EBA(PPh_3)_2$
26,300	26,500	26,700
$2.1x10^3$	$2.0x10^3$	$2.7x10^3$
23,600	22,600	21,900
$2.3x10^3$	$2.5x10^3$	$4.1x10^3$
19,300	19,400	19,800
$7.0x10^2$	$7.0x10^2$	$2.0x10^3$

$ReC\ell_2HFAA(PPh_3)_2$	$ReBr_2HFAA(PPh_3)_2$	$ReI_2HFAA(PPh_3)_2$
38,000	37,600	37,000
$6.2x10^3$	$6.7x10^3$	$8.2x10^3$
33,300	32,500	26,000
$2.9x10^3$	$3.4x10^3$	$2.3x10^3$
25,400	23,500	21,300
$3.1x10^3$	$2.8x10^3$	$2.7x10^3$
20,400	20,200	19,500
$3.2x10^3$	$2.5x10^3$	$2.2x10^3$
15,500	16,000	16,000
$1.7x10^3$	$1.8x10^3$	$1.8x10^3$

$ReC\ell_2TFBA(PPh_3)_2$	$ReBr_2TFBA(PPh_3)_2$	$ReI_2TFBA(PPh_3)_2$
38,200	38,800	37,000
$7.3x10^3$	$1.1x10^4$	$1.6x10^4$
37,300		
$7.7x10^3$		
36,300		
$7.7x10^3$		
35,000	34,200	33,300
$6.9x10^3$	$6.3x10^3$	$8.5x10^3$
32,800		27,000
$6.4x10^3$		$4.7x10^3$

TABLE 21 continued

$ReC\ell_2TFBA(PPh_3)_2$	$ReBr_2TFBA(PPh_3)_2$	$ReI_2TFBA(PPh_3)_2$
25,600	23,300	
$2.4x10^3$	$1.7x10^3$	
24,000	21,600	20,600
$1.7x10^3$	$2.5x10^3$	$5.9x10^3$
19,800	20,800	18,600
$2.6x10^3$	$2.3x10^3$	$4.4x10^3$
15,500	16,300	16,300
$2.7x10^3$	$2.1x10^3$	$3.6x10^3$

$ReC\ell_2TFTA(PPh_3)_2$	$ReBr_2TFTA(PPh_3)_2$	$ReI_2TFTA(PPh_3)_2$
37,900	37,500	37,500
$8.0x10^3$	$6.5x10^3$	$8.3x10^3$
37,300		
$8.4x10^3$		
36,400	36,500	36,400
$8.0x10^3$	$7.5x10^3$	$7.5x10^3$
31,300	31,500	32,900
$9.1x10^3$	$8.2x10^3$	$6.4x10^3$
27,400	27,000	27,200
$3.2x10^3$	$2.7x10^3$	$3.4x10^3$
25,800	24,300	24,900
$2.7x10^3$	$2.9x10^3$	$2.7x10^3$
20,500	20,500	21,000
$3.6x10^3$	$1.8x10^3$	$2.2x10^3$
19,100	19,100	19,100
$3.6x10^3$	$3.1x10^3$	$2.5x10^3$
14,800	15,000	15,000
$3.3x10^3$	$3.4x10^3$	$2.3x10^3$

were not available as the compounds, especially iodide analogues, could not be prepared in sufficient quantity.

The predicted value for the magnetic susceptibility of octahedral Re(III) compounds was obtained using the following equation, -

$$\chi_M = \frac{2N\beta^2(1+\cos\Theta)(2+\kappa)^2}{3\delta(8^{-1/2}\tan\Theta-1+\sec\Theta)} \qquad (5)$$

where $\delta = 1/2(15B+5C+\zeta')\kappa$

$\tan\Theta = 2^{1/2}\zeta'/\delta$

and $\zeta' >> kT$

$0.7 \leq \kappa \leq 1$

This equation was used by Earnshaw et al. (41), to predict the susceptibilities of similar Re(III) compounds. It gives $\overset{\circ}{\chi}_{Re} = 1640 \times 10^{-6}$ c.g.s.u. (susceptibility at zero degrees Kelvin). To this, a correction of 60×10^{-6} c.g.s.u. must be added to account for the second order Zeeman effect (41). Because of the large spin orbit coupling involved (41), the susceptibility should be independent of temperature. This gives a value about 1700×10^{-6} c.g.s.u. for octahedral Re(III)

The same sort of small, erratic variation of susceptibility with temperature that is seen in FIGURES 11-17 was observed by Earnshaw et al. (41) in the series of Re(III) complexes they studied. Moreover, the magnitude of the susceptibilities are comparable.

This irregular behaviour may be caused by the non-octahedral symmetry of the $ReX_2dik(PPh_3)_2$ compounds. The structure of $ReC\ell_2AA(PPh_3)_2$ has been determined and is given in FIGURE 4. Although essentially an octahedral array of ligand atoms exists around the rhenium, there are three different types of ligand

FIGURE 11

Plot of χ versus T for $ReX_2AA(PPh_3)_2$ compounds

data for Cℓ compounds ○

data for Br compounds □

data for I compounds △

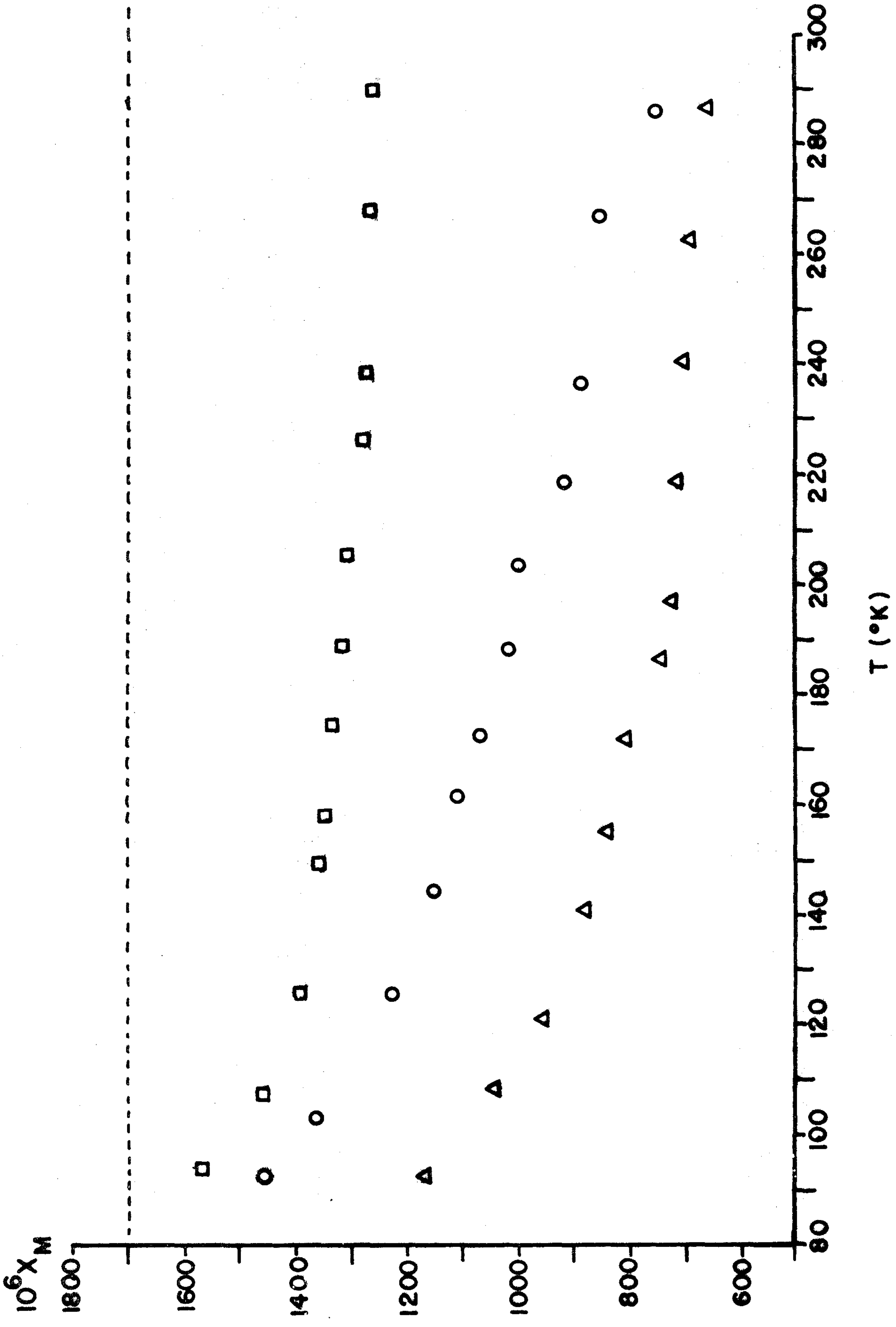

$10^6 \chi_M$
1800
1600
1400
1200
1000
800
600
80
100
120
140
160
180
200
220
240
260
280
300
T (°K)

FIGURE: 11

FIGURE 12

Plot of χ versus T for $ReX_2HFAA(PPh_3)_2$ compounds

data for Cℓ compounds ○

data for Br compounds □

data for I compounds △

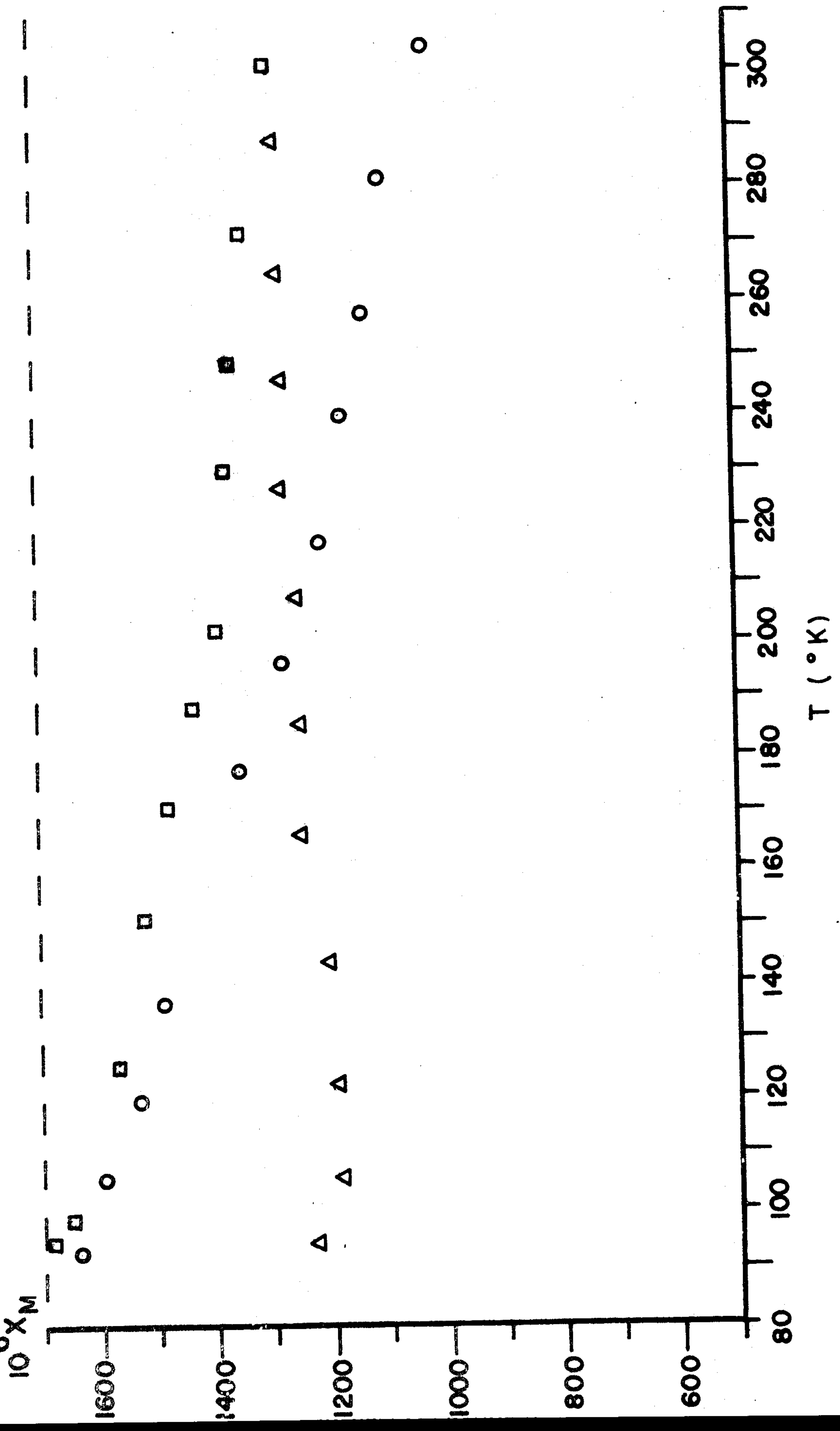

$10^6\chi_M$
1600
1400
1200
1000
800
600
80
100
120
140
160
180
200
220
240
260
280
300
T (°K)

FIGURE: 12

FIGURE 13

Plot of χ versus T for $\mathrm{ReX_2EAA(PPh_3)_2}$ compounds

data for Cℓ compounds ○

data for Br compounds □

data for I compounds △

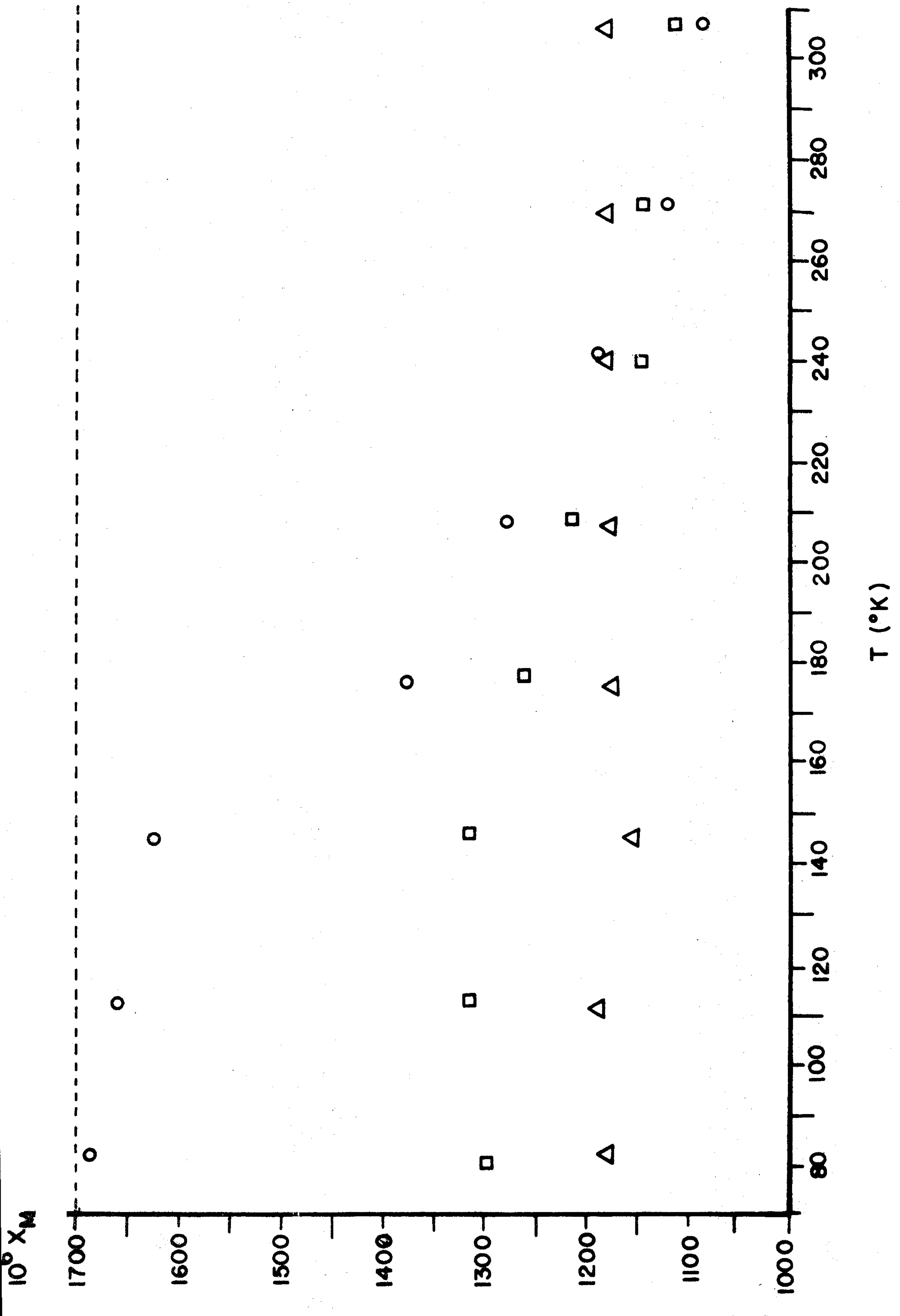

$10^6 X_M$
1700
1600
1500
1400
1300
1200
1100
1000
80
100
120
140
160
180
200
220
240
260
280
300
T (°K)

FIGURE: 13

FIGURE 14

Plot of χ versus T for $ReX_2DBM(PPh_3)_2$ compounds

data for Cℓ compounds ○

data for Br compounds □

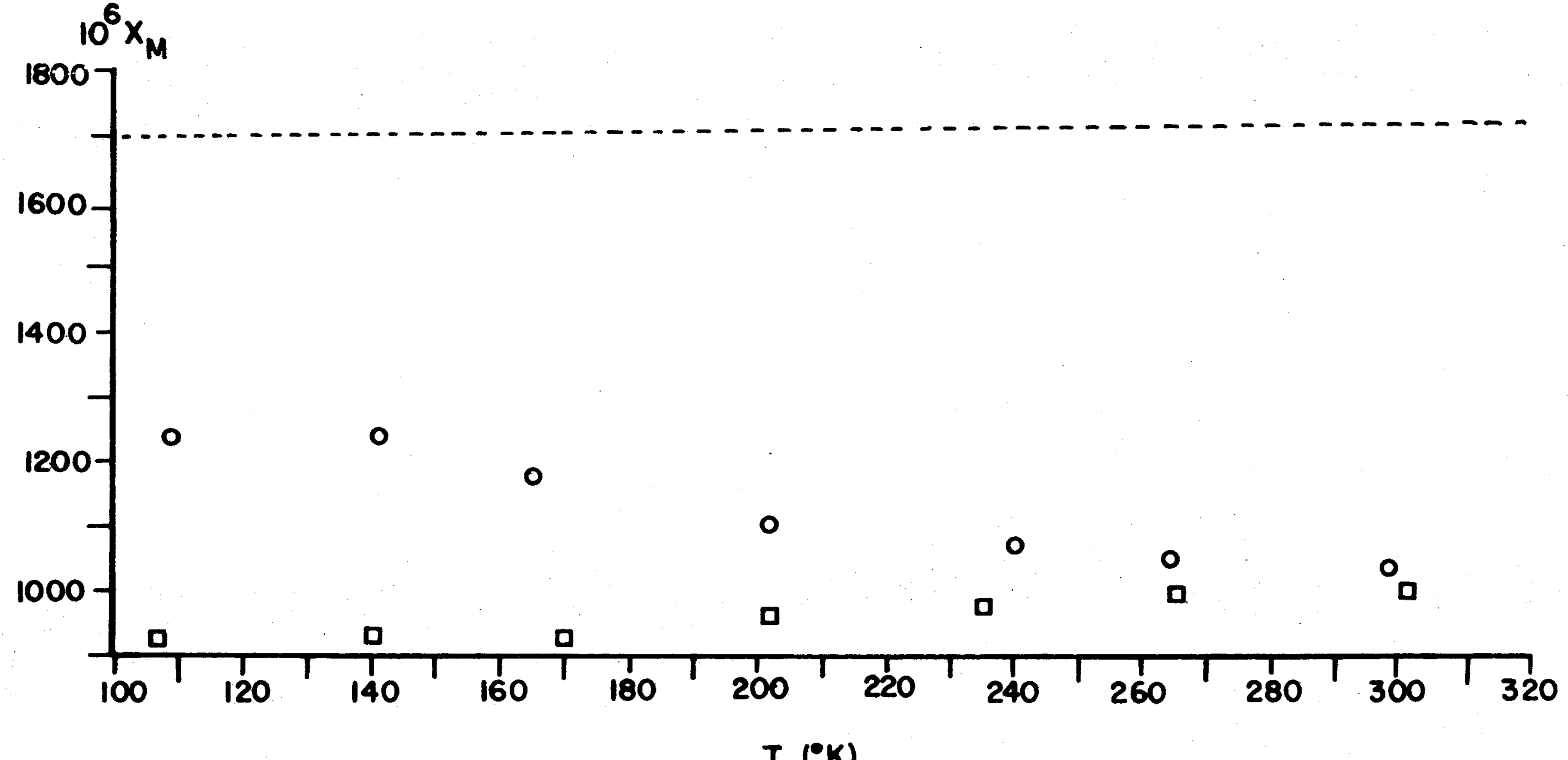

$10^6 X_M$
1800
1600
1400
1200
1000
100
120
140
160
180
200
220
240
260
280
300
320
T (°K)

FIGURE : 14

FIGURE 15

Plot of χ versus T for $ReX_2EBA(PPh_3)_2$ compounds

data for Cℓ compounds ○

data for Br compounds ☐

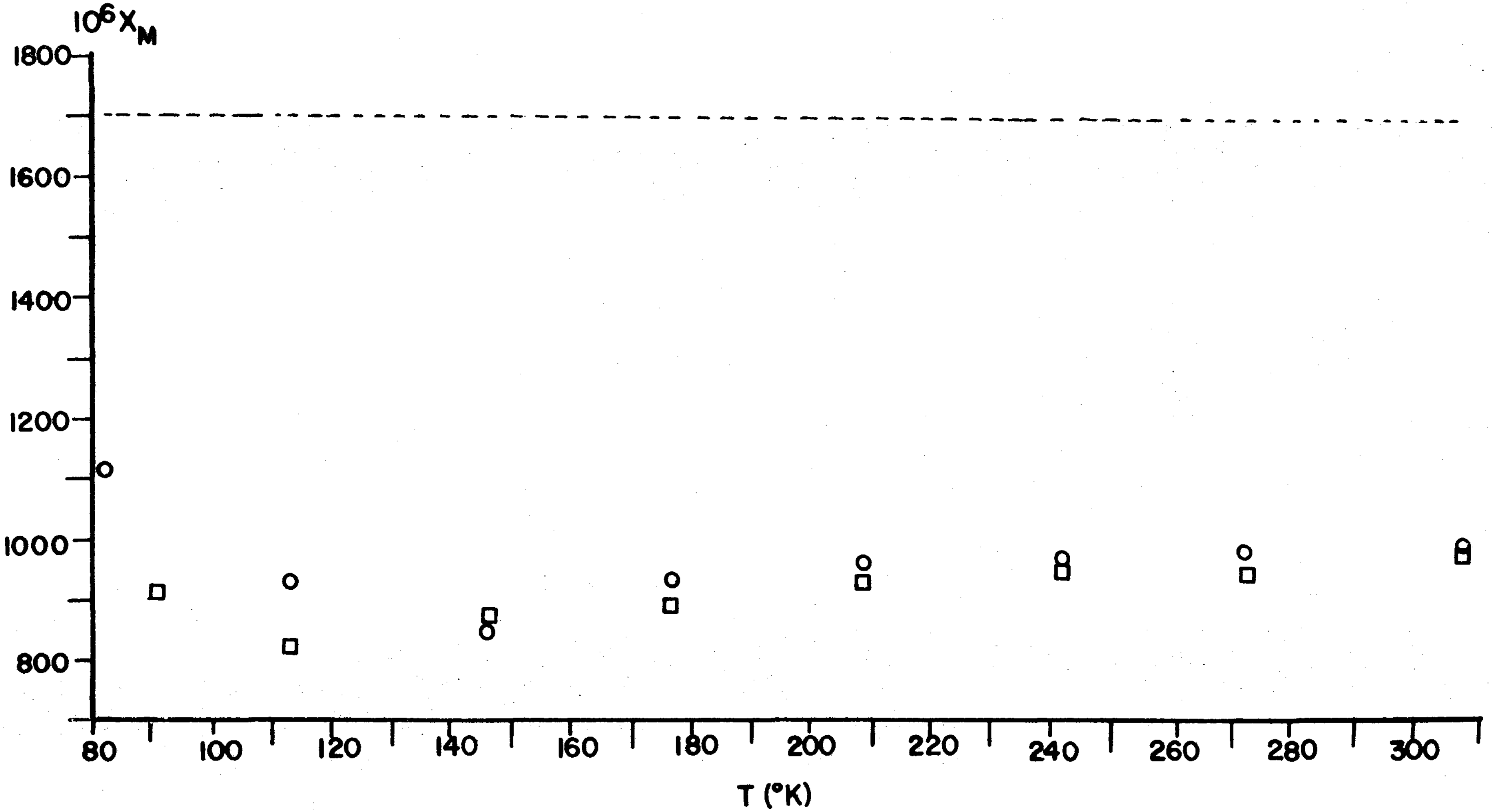

$10^6 \chi_M$
1800
1600
1400
1200
1000
800
80
100
120
140
160
180
200
220
240
260
280
300
T (°K)

FIGURE: 15

FIGURE 16

Plot of χ versus T for $ReX_2TFBA(PPh_3)_2$ compounds

data for Cℓ compounds ○

data for Br compounds □

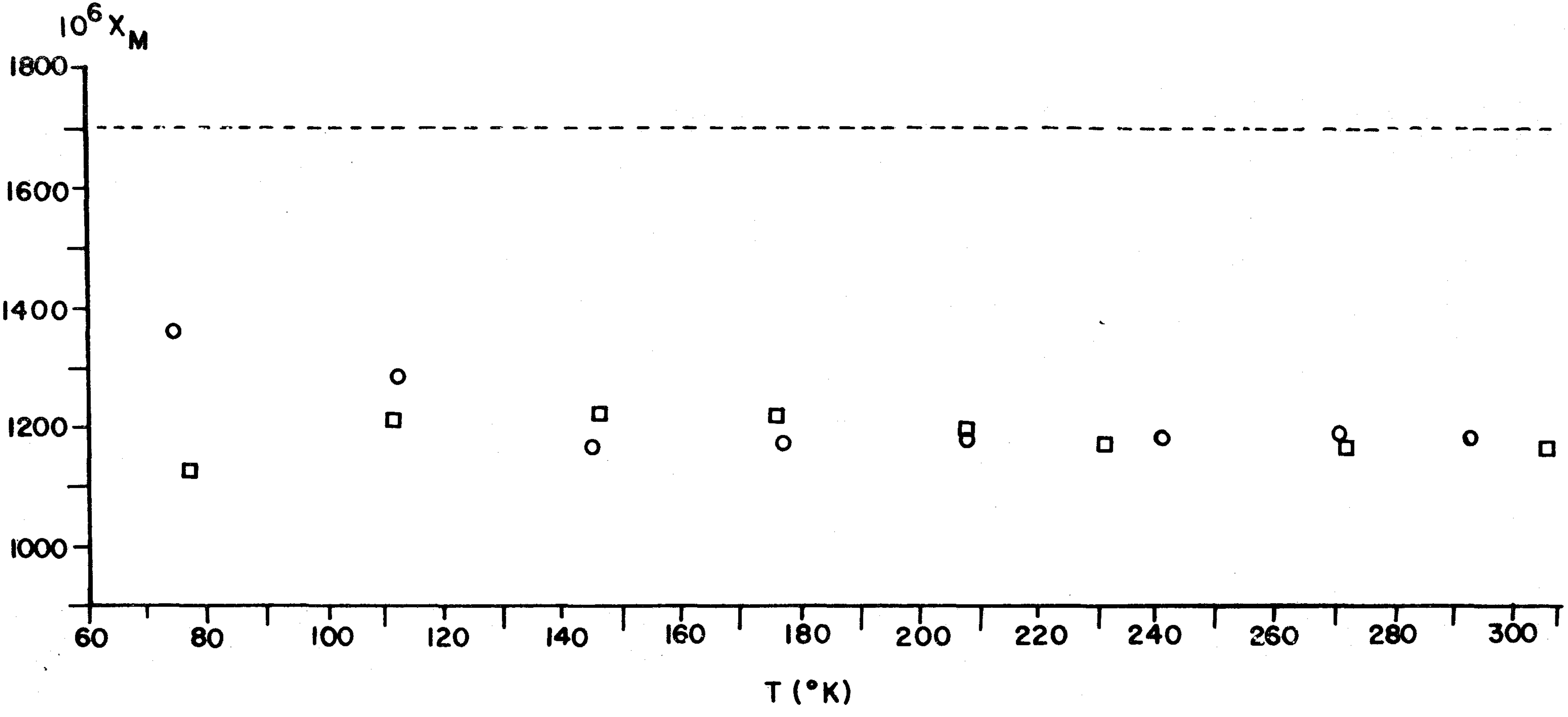

$10^6 X_M$
1800
1600
1400
1200
1000
60
80
100
120
140
160
180
200
220
240
260
280
300
T (°K)

FIGURE: 16

FIGURE 17

Plot of χ versus T for $ReX_2TFTA(PPh_3)_2$ compounds

data for Cℓ compounds ○

data for Br compounds □

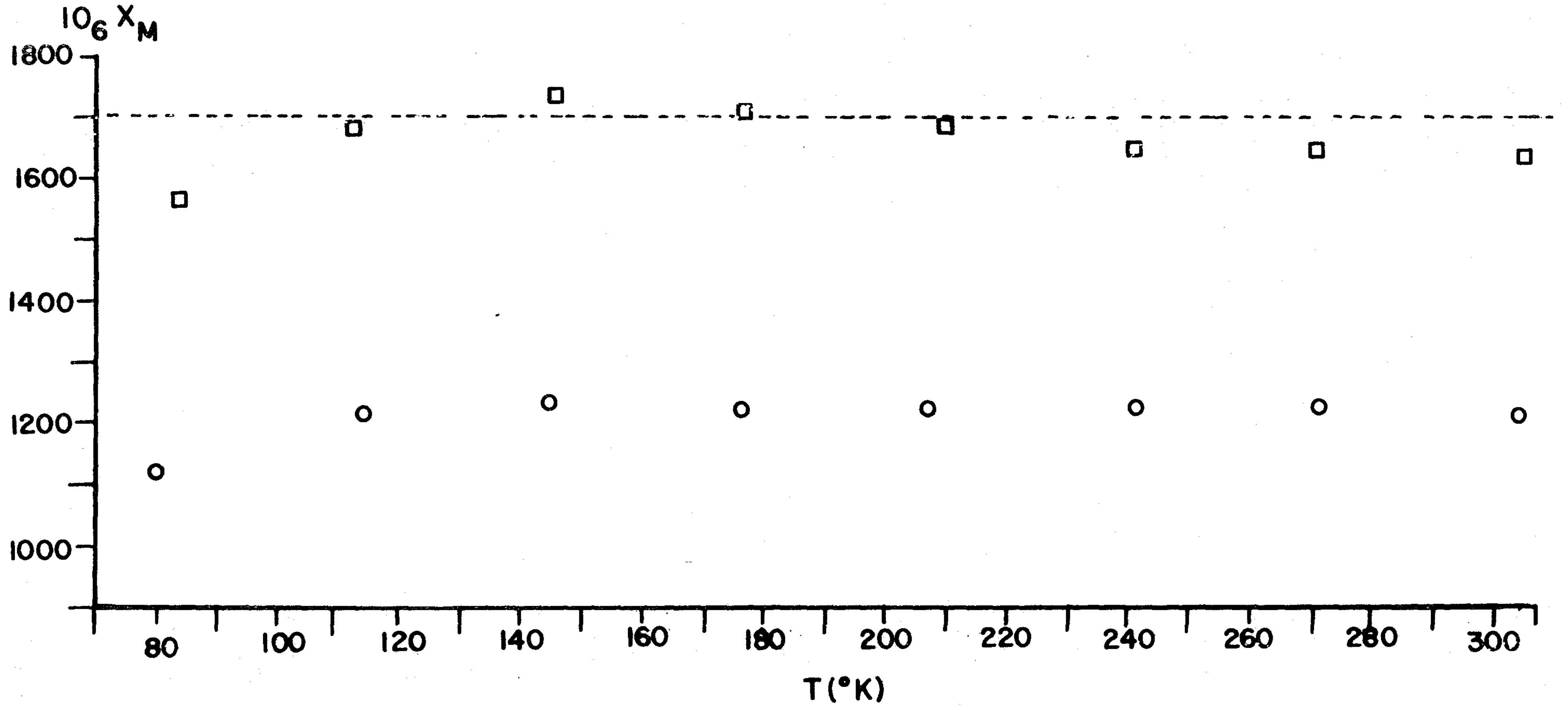

$10^6 \chi_M$
1800
1600
1400
1200
1000
80
100
120
140
160
180
200
220
240
260
280
300
T(°K)

FIGURE: 17

atoms, chlorine, oxygen and phosphorus and the oxygens form part of a chelate ring. It will be seen in Chapter 6 that for the symmetrical tris compounds, very little variation of susceptibility with temperature is observed.

The close similarities in behaviour of the compounds listed in TABLE 20 have prompted the conclusion that they are members of the same series. Moreover, the structure of $ReC\ell_2AA(PPh_3)_2$ given in FIGURE 4, Chapter 1, is probably typical of the series.

These compounds will provide precursors to tris compounds of the type $Re(dik)_3$ and perhaps to compounds of the type $Re(dik)(dik')_2$.

2. Related Rhenium (III) Compounds

Two compounds similar to $ReC\ell_2AA(PPh_3)_2$ have been isolated in which one of the phosphines has been replaced by another group. Substitution of triphenylphosphine oxide for triphenylphosphine gives dichloropentane-2,4-dionatotriphenylphosphineoxidetriphenylphosphinerhenium(III), $ReC\ell_2AAOPPh_3PPh_3$. Substitution of pyridine for triphenylphosphine gives dichloropentane-2,4-dionatopyridinetriphenylphosphinerhenium(III), $ReC\ell_2AApyPPh_3$.

Spectral data in the ultraviolet visible region and magnetic susceptibility data for $ReC\ell_2AA(PPh_3)_2$, $ReC\ell_2AAOPPh_3PPh_3$ and $ReC\ell_2AApyPPh_3$ are compared in TABLES 22 and 23.

The compounds $ReC\ell_2AA(PPh_3)_2$ and $ReC\ell_2AAOPPh_3PPh_3$ show very similar properties while $ReC\ell_2AApyPPh_3$ differs slightly from the other two.

The compound $ReC\ell_2AApyPPh_3$ is the first reported rhenium compound that has both a β-diketonate and a pyridine ligand. Attempts to prepare such compounds from pyridine-containing starting materials have failed (42).

TABLE 22

Electronic Spectra of $ReC\ell_2AA(PPh_3)_2$, $ReC\ell_2AAOPPh_3PPh_3$ and $ReC\ell_2AApyPPh_3$

$ReC\ell_2AA(PPh_3)_2$	$ReC\ell_2AAOPPh_3PPh_3$	$ReC\ell_2AApyPPh_3$
39,000 cm^{-1}	37,900 cm^{-1}	36,300
$1.1x10^4$	$5.0x10^3$	$6.1x10^3$
33,800	37,300	
$3.9x10^3$	$5.3x10^3$	
29,000	36,200	
$2.6x10^3$	$5.0x10^3$	
23,600	26,800	26,800
$1.9x10^3$	$2.8x10^3$	$2.7x10^3$
20,400	19,600	20,100
$6.2x10^2$	$1.0x10^3$	$1.3x10^3$

TABLE 23

Magnetic Susceptibilities of $ReC\ell_2AA(PPh_3)_2$, $ReC\ell_2AAOPPh_3PPh_3$ and $ReC\ell_2AApyPPh_3$

$ReC\ell_2AA(PPh_3)_2$		$ReC\ell_2AAOPPh_3PPh_3$		$ReC\ell_2AApyPPh_3$	
T°K	$10^6\chi_M$ c.g.s.u.	T°K	$10^6\chi_M$ c.g.s.u.	T°K	$10^6\chi_M$ c.g.s.u.
93	1455	93	1618	93	1356
103	1371	100	1480	109	1342
126	1225	117	1371	123	1336
145	1149	149	1293	141	1339
173	1072	176	1257	172	1348
219	919	210	1238	206	1345
236	891	248	1226	244	1348
267	856	259	1226	266	1356
307	843	295	1178	302	1359

The compound was prepared by reacting pyridine with either $ReC\ell_2AA(PPh_3)_2$ or $ReC\ell_2AAOPPh_3PPh_3$. This reaction proved very helpful in the elucidation of the reaction sequence described in Chapter 5.

CHAPTER 5

REACTION SCHEME

A previous attempt to relate the several compounds produced in the reaction between acetylacetone and $ReO(OR)C\ell_2(PPh_3)_2$ dealt with the reaction that occurred in benzene solution (13). Three products were claimed: $ReOC\ell_2AAPPh_3$, $ReC\ell_2AA(PPh_3)_2$ and $Re(AA)_3$. (see Introduction for reaction scheme). In this work, $Re(AA)_3$ was never isolated from such a reaction. Indeed the characteristics of authentic $Re(AA)_3$ (Chapter 6) almost preclude its being isolated from a reaction of this sort. Rather, it would be more likely to be oxidized.

It has been shown in this work (Experiments Section 9) and elsewhere (20,21) that the group trans to a double bonded oxygen-rhenium system, Re=O, is very labile.

The first step in the reaction of acetylacetone with trans-$ReO(OMe)C\ell_2(PPh_3)_2$ is probably dissociation of the rhenium-containing reactant to $[ReOC\ell_2(PPh_3)_2]^+$, a five-coordinate species. Attack by the enol form of acetylacetone (43) at the vacant sixth coordination position would give a proton and $[ReOC\ell_2AA(PPh_3)_2]$ in which the acetylacetonate anion is coordinated through only one of its oxygens. Chelation would be accomplished by liberating a triphenylphosphine and replacing it with the remaining oxygen of the acetylacetonate anion. The H^+ could be taken up by the methoxy anion to give methanol.

The enol form of acetylacetone is most probably involved because sodium acetylacetonate reacts in a similar fashion giving $ReC\ell_2AA(PPh_3)_2$.

It is impossible, however, to stop the sodium acetylacetonate reaction at the product $ReOC\ell_2AAPPh_3$. In addition, acetylacetone at ambient temperatures is 84% enol-form (43), from which a metal chelate is easily formed (Introduction).

The most significant feature of the product, $ReOC\ell_2AAPPh_3$, is the short distance (in the solid state) between the phosphorus and the oxygen of the Re=O system. This distance is less than the sum of the Van der Waals radii for phosphorus and oxygen (17).

The subsequent product, $ReC\ell_2AAOPPh_3PPh_3$, is a Re(III) compound that has a triphenylphosphine oxide group (P(V)) in it. It was thought that an intramolecular oxidation-reduction reaction might be involved because of the proximity of the phosphorus and oxygen in $ReOC\ell_2AAPPh_3$, mentioned above. Such a process would involve the phosphorus of the triphenylphosphine bonded to Re(V), in $ReOC\ell_2AAPPh_3$, moving to the oxygen of the Re=O system and being oxidized to give a coordinated triphenylphosphine oxide while the rhenium was reduced to Re(III). Then, a second molecule of triphenylphosphine (left from the production of $ReOC\ell_2AAPPh_3$) could complete the six coordination of the rhenium. However, experiments with $ReOC\ell_2AAPPh_3$ and diphenylmethylphosphine suggested that the phosphine oxide in the resulting compound was diphenylmethylphosphine oxide (Experiments Section 6.3). Unfortunately, it was not possible to prepare $ReOC\ell_2AAPMePh_2$ to investigate the reaction with triphenylphosphine.

The reduction seems then, to be accomplished by the attack of triphenylphosphine on the double-bonded oxygen to give coordinated triphenylphosphine oxide and Re(III).

In the presence of more triphenylphosphine, the triphenylphosphine oxide is replaced by a triphenylphosphine group to give $ReC\ell_2AA(PPh_3)_2$.

Implicit in the two steps just described are the assumptions that $ReC\ell_2AAOPPh_3PPh_3$ can have cis triphenylphosphine and triphenylphosphine oxide groups and that the oxygen double bonded to the rhenium in the compound $ReOC\ell_2AAPPh_3$ and thus from the starting material $ReO(OMe)C\ell_2(PPh_3)_2$ is the one bonded to the phosphorus in the coordinated triphenylphosphine oxide group of the compound $ReC\ell_2AAOPPh_3PPh_3$. The first assumption is not unreasonable because rhodium compounds with cis-triphenylphosphine groups are known e.f. $RhC\ell(PPh_3)_3$, though they are not particularly stable in solution (44). The steric problems encountered in a cis-triphenylphosphine situation would probably be much greater than for cis-triphenylphosphine-triphenylphosphine oxide. The second assumption could clearly be validated by the use of O^{18} in the starting material. However, the oxygen of the Re=O system in $ReO(OMe)C\ell_2(PPh_3)_2$ comes from the perrhenate formed by treating rhenium metal with hydrogen peroxide. The preparation of $ReO^{18}(OMe)C\ell_2(PPh_3)_2$ would certainly be tedious and probably very difficult.

As indirect proof of the validity of the two assumptions are offered the observations that triphenylphosphine oxide cannot be produced from triphenylphosphine and acetylacetone under the conditions of the reaction (refluxing in a nitrogen atmosphere) and that under these conditions triphenylphosphine oxide cannot be made to react with $ReOC\ell_2AAPPh_3$.

The yield of $ReC\ell_2AA(PPh_3)_2$ from this reaction is always less than 50%. Therefore, the initial conversion of $ReO(OMe)C\ell_2(PPh_3)_2$ to $ReOC\ell_2AAPPh_3$, which is almost quantitative, provides enough triphenylphosphine for the next two steps.

It should be mentioned here that by stopping the reaction in neat acetylacetone at the appropriate point, $ReOC\ell_2AAPPh_3$, $ReC\ell_2AAOPPh_3PPh_3$ and $ReC\ell_2AA(PPh_3)_2$ can be isolated as in the "benzene as solvent" reaction described in (13) and the Experiments Section 8. Moreover, both $ReC\ell_2AAOPPh_3PPh_3$ and $ReC\ell_2AA(PPh_3)_2$ could be prepared from $ReOC\ell_2AAPPh_3$ by treatment with an appropriate amount of triphenylphosphine. Treatment of $ReC\ell_2AAOPPh_3PPh_3$ with triphenylphosphine gave $ReC\ell_2AA(PPh_3)_2$. Acetone and/or benzene were used as solvents for these reactions to facilitate the isolation and purification of the products.

Any of the three compounds, $ReOC\ell_2AAPPh_3$, $ReC\ell_2AAOPPh_3PPh_3$ or $ReC\ell_2AA(PPh_3)_2$ could be converted to $ReC\ell_2(AA)_2$ by further treatment with neat acetylacetone.

TABLE 24 provides an outline of the reactions discussed and approximate yields of the products isolated. The low yield of $ReC\ell_2(AA)_2$ in the last reaction listed may be indicative of undiscovered side reactions of one or more of the intermediates involved.

If this reaction is run longer (up to 60 hrs.) the yield increases and this is taken to be indicative of further reaction of the $ReC\ell_2AA(PPh_3)_2$ produced.

No further reaction of $ReC\ell_2(AA)_2$ with acetylacetone was observed even after refluxing for two weeks. It seems unlikely, therefore, that '$Re(AA)_3$' reported previously (13) is a product of this reaction; rather it may be the product of a different or side reaction between acetylacetone and one or more of the intermediates isolated. Authentic $Re(AA)_3$ may be prepared in low yield by destructively distilling

TABLE 24

Reactants	Conditions	Products
$ReO(OMe)C\ell_2(PPh_3)_2$ + HAA	$\xrightarrow[\text{48 hrs}]{\Delta}$	$(ReOC\ell_2AAPPh_3)$, $(ReC\ell_2AAOPPh_3PPh_3)$, $(ReC\ell_2AA(PPh_3)_2 \rightarrow$ $ReC\ell_2(AA)_2$ 33%
$ReO(OMe)C\ell_2(PPh_3)_2$ + HAA	$\xrightarrow[\text{Acetone 12 hrs}]{\text{stir @ Room Temp}}$	$ReOC\ell_2AAPPh_3$ 75% $ReO(OMe)C\ell_2(PPh_3)_2$ 20%
$ReO(OMe)C\ell_2(PPh_3)_2$ + HAA	$\xrightarrow[\text{Acetone 4 hrs}]{\Delta}$	$ReOC\ell_2AAPPh_3$ 22% $ReC\ell_2AAOPPh_3PPh_3$ 67% $ReC\ell_2AA(PPh_3)_2$ trace
$ReO(OMe)C\ell_2(PPh_3)_2$ + HAA	$\xrightarrow[\text{Acetone 12 hrs}]{\text{stir @ Room Temp}}$	$\xrightarrow[\text{Acetone 4 hrs}]{\Delta}$ $ReOC\ell_2AAPPh_3$ 40% $ReC\ell_2AAOPPh_3PPh_3$ 30% $ReO(OMe)C\ell_2(PPh_3)_2$ 25%
$ReO(OMe)C\ell_2(PPh_3)_2$ + HAA	$\xrightarrow[\text{benzene 6 hrs}]{\Delta}$	$ReOC\ell_2AAPPh_3$ 29% $ReC\ell_2AA(PPh_3)_2$ 42% $ReC\ell_2AAOPPh_3PPh_3$ trace
$ReOC\ell_2AAPPh_3$ + HAA	$\xrightarrow[\text{12 hrs}]{\Delta}$	$ReC\ell_2(AA)_2$ 58%
$ReC\ell_2AAPPh_3OPPh_3$ + HAA	$\xrightarrow[\text{12 hrs}]{\Delta}$	$ReC\ell_2(AA)_2$ 69%
$ReC\ell_2AA(PPh_3)_2$ + HAA	$\xrightarrow[\text{12 hrs}]{\Delta}$	$ReC\ell_2(AA)_2$ 39%
$ReO(OMe)C\ell_2(PPn_3)_2$ + HAA	$\xrightarrow[\text{12 hrs}]{\Delta}$	$ReC\ell_2(AA)_2$ 26% + $OPPh_3$ + $ReC\ell_2(AA)(PPh_3)_2$

Note: Yields in these reactions vary by up to 20% between consecutive identical preparations. The percentages are included only to reflect whether or not the product isolated is the major component.

a mixture of $ReC\ell_2(AA)(PPh_3)_2$ or $ReC\ell_2(AA)_2$ and NaAA.

The product $ReC\ell(AA)_2PPh_3$ described by Grove et al (4) was never encountered in this work. Indeed deliberate attempts to produce it by the method described (4) were unsuccessful. It may be visualized simply as a product obtained by further substitution of $ReC\ell_2AA(PPh_3)_2$ by AA. That is to say, loss of a PPh_3 and Cl and incorporation of AA to give $ReC\ell(AA)_2PPh_3$.

The reaction sequence is depicted in FIGURES 18, 19, 20, 21 and 22.

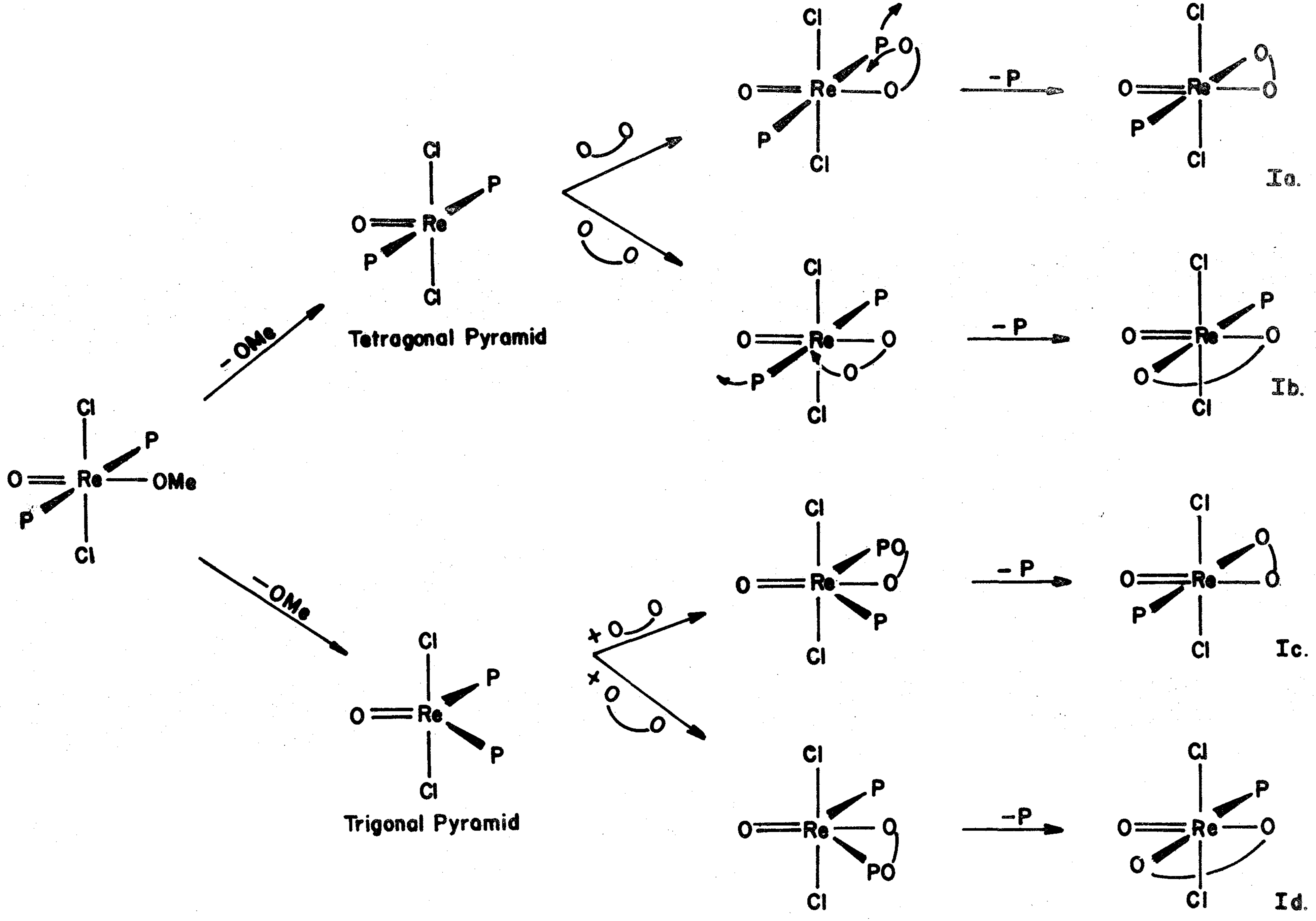
A dissociative mechanism has been chosen to describe these reactions. Examination of models of the compounds under consideration revealed that displacement type reactions with seven-coordinate intermediates would meet considerable steric hinderance. Moreover, in the case of $ReO(OMe)C\ell_2(PPh_3)_2$, the lability of the group trans to the Re=O system is best described in terms of a dissociative process. Furthermore, for compounds of Type III, the results of osmometric molecular weight determinations are consistently low, indicating partial dissociation.

In FIGURE 18, both tetragonal pyramidal and trigonal bipyramidal intermediates are shown. "These two structures appear to be the most plausible ones because (1) stable compounds of such structures are known, (2) these structures can be derived from the octahedron with little atomic motion and (3) such structures are in keeping with current theories of bonding in metal complexes" (45). As indicated, both intermediate structures give a product of Type I with the same stereochemistry.

In FIGURE 19, the reduction of Re(V) to Re(III) by a triphenylphosphine group is straightforward. This Type II product is

FIGURE 18

Reaction scheme for the production of $ReOC\ell_2AAPPh_3$ from $ReO(OMe)C\ell_2PPh_3$ and acetylacetone.



Cl
O=Re—OMe
P
-OMe
Tetragonal Pyramid
Trigonal Pyramid
+O
-P
PO
Ia.
Ib.
Ic.
Id.

FIGURE: 18

FIGURE 19

Reaction scheme for the conversion of $\mathrm{ReOC\ell_2AAPPh_3}$ to $\mathrm{ReC\ell_2AAOPPh_3PPh_3}$ and $\mathrm{ReC\ell_2AA(PPh_3)_2}$ by reaction with triphenylphosphine

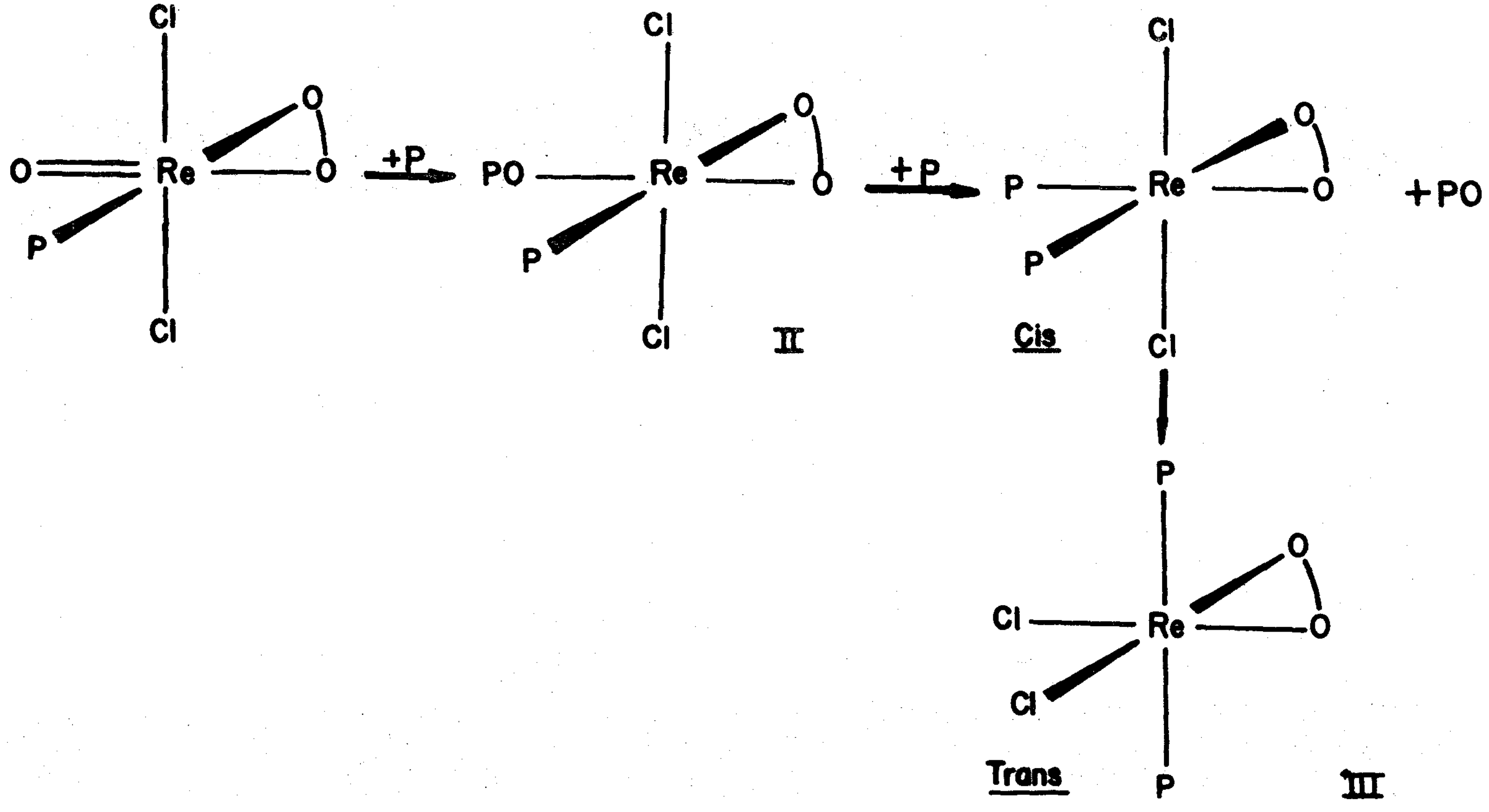


FIGURE: 19

FIGURE 20

Reaction scheme for the conversion of $ReOC\ell_2AAPPh_3$ to $ReC\ell_2(AA)_2$ by reaction with triphenylphosphine and acetylacetone

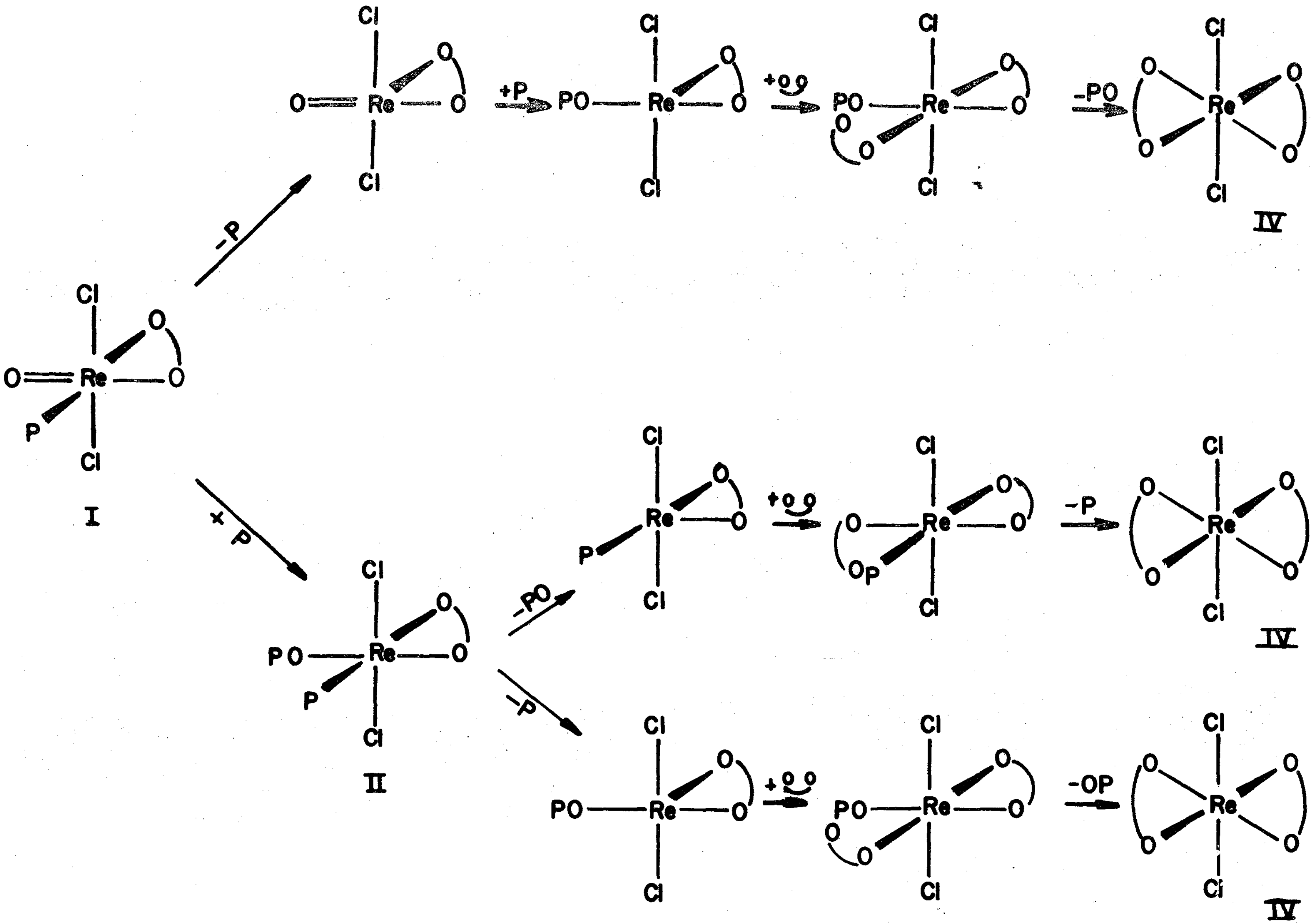


FIGURE: 20

FIGURE 21

Reaction scheme for the conversion of $ReC\ell_2AA(PPh_3)_2$ to $ReC\ell_2(AA)_2$ by reaction with acetylacetone

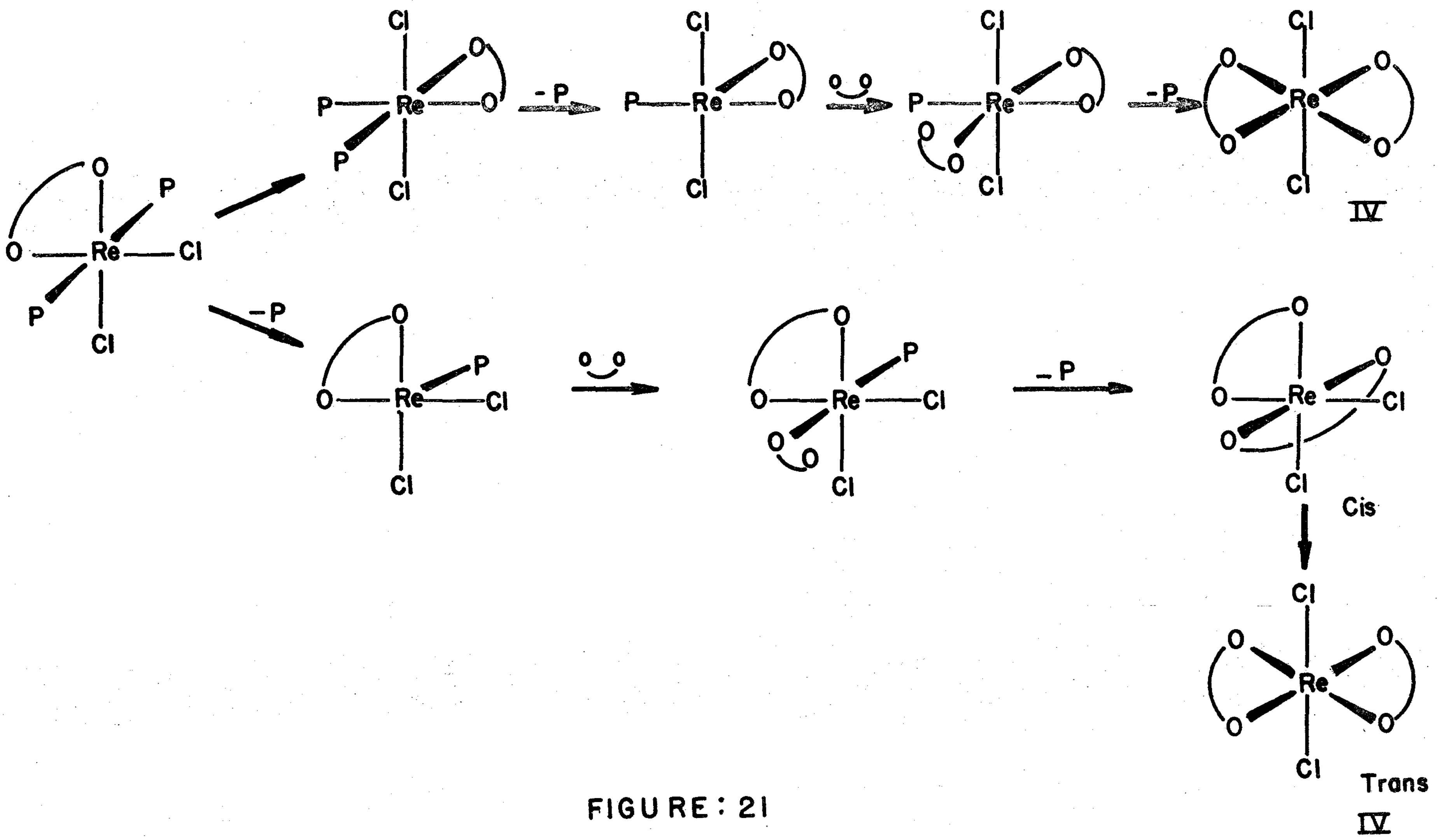


FIGURE: 21

FIGURE 22

Reaction scheme for the $ReO(OMe)C\ell_2(PPh_3)_2$ - acetylacetone system

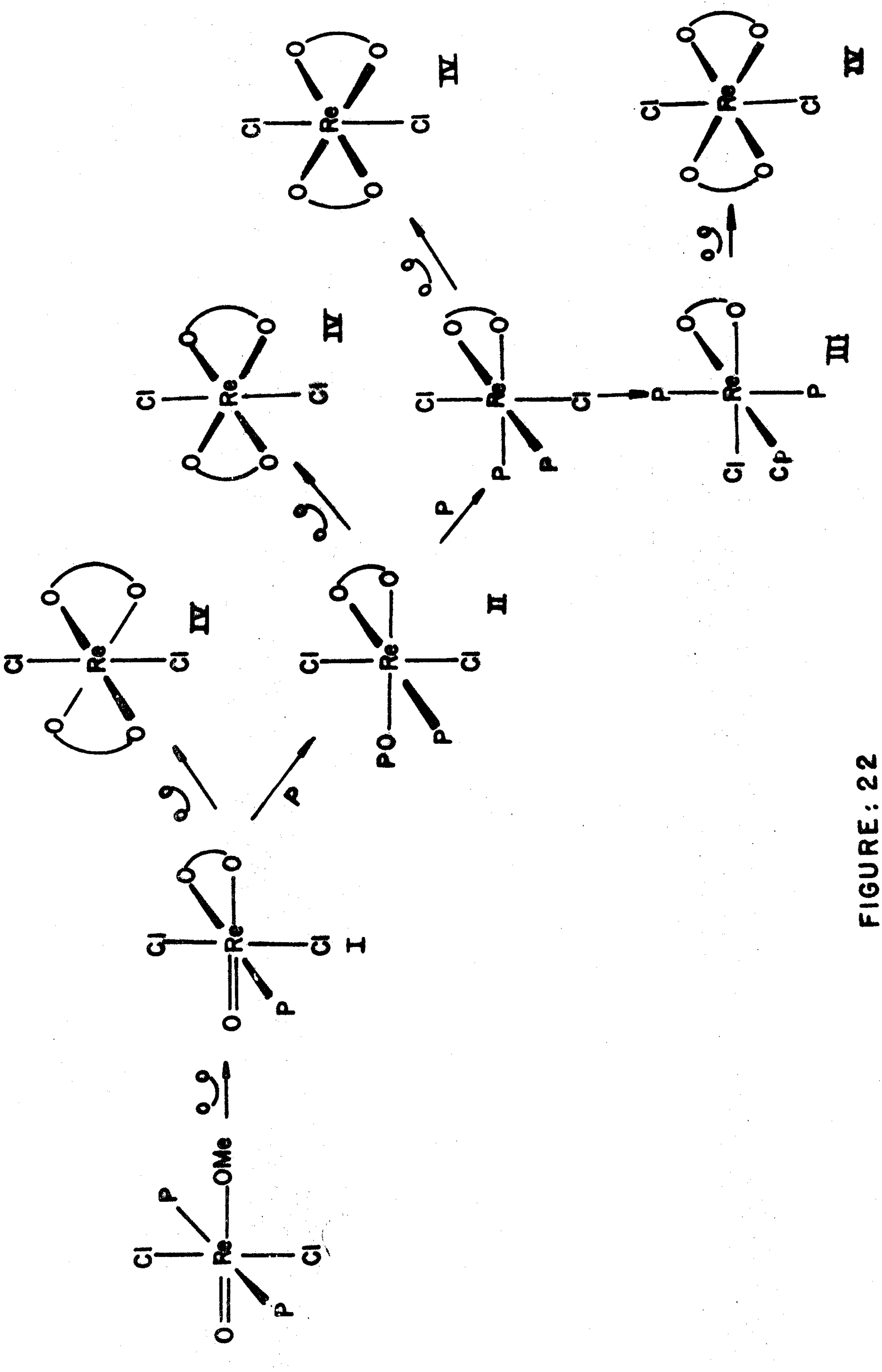


FIGURE: 22

assumed to have cis triphenylphosphine and triphenylphosphine oxide groups. No structural information is available for this compound so an unambiguous assignment of stereochemistry is impossible. However, the conversion of product I to product II is quite facile and quick. There is no simple dissociative isomerization process that could convert the cis form into the trans in this case. The chelating acetylacetonate group blocks the attack point for such a process and a reaction which involved breaking up the chelated Re-AA system would not be expected to proceed so readily.

Product III has trans triphenylphosphine groups. Again there is no simple mechanism to explain such a product. The triphenylphosphine oxide could easily be replaced by the better base, triphenylphosphine but the resulting compound would have cis triphenylphosphine groups. The trans triphenylphosphine product precipitates from the reaction solution and this may displace an equilibrium between the two forms in favour of the trans form. Moreover, an examination of models of the compounds suggests considerably less steric hinderance for the trans-form.

FIGURES 20 and 21 depict the formation of $ReC\ell_2(AA)_2$ from $ReOC\ell_2AAPPh_3$, $ReC\ell_2AAOPPh_3PPh_3$ and $ReC\ell_2AA(PPh_3)_2$.

The reaction between acetylacetone and $ReOC\ell_2AAPPh_3$ as depicted proceeds via a Re(III) intermediate. Attack by the enol form of acetylacetone follows but the intermediate is neutral, not charged as in the first reaction (FIGURE 18) and oxidation to Re(IV) takes place and triphenylphosphine oxide is liberated leaving trans-$ReC\ell_2(AA)_2$.

The reaction between $ReC\ell_2AAOPPh_3PPh_3$ and acetylacetone involves an intermediate similar to that mentioned above but having a triphenylphosphine group instead of triphenylphosphine oxide. Triphenylphosphine oxide is a poorer ligand than triphenylphosphine and would be expected to come off easier. Neither the triphenylphosphine nor the triphenylphosphine oxide are present in the final product so it really doesn't matter which comes off first. Attack by the enol form of acetylacetone occurs as described before and oxidation of the Re(III) to Re(IV) and the liberation of triphenylphosphine gives trans-$ReC\ell_2(AA)_2$.

There must be a rearrangement involved in the conversion of trans-$ReC\ell_2AA(PPh_3)_2$ to trans-$ReC\ell_2(AA)_2$. The simple dissociative mechanism used in the previous two cases leads to a cis-chloro-product. The mechanism depicted in FIGURE 21 involves a rearrangement of cis-$ReC\ell_2(AA)_2$ to trans-$ReC\ell_2(AA)_2$. Alternatively, the rearrangement of the starting product trans-$ReC\ell_2AA(PPh_3)_2$ to cis-$ReC\ell_2AA(PPh_3)_2$ could occur (cis and trans refer here to the spatial relationships between the triphenylphosphine groups). The isolation of small amounts of cis-$ReC\ell_2AA_2$ (Chapter 3) provides evidence for choosing the rearrangement of the Re(IV) compound.

The complete reaction is summarized in FIGURE 22. In order to simplify the scheme, the cis-trans isomerism of $ReC\ell_2(AA)_2$ has been omitted from the figure.

CHAPTER 6

TRIS β-KETOENOLATE COMPLEXES OF RHENIUM

Two tris β-diketonate complexes of rhenium have been reported (11a, b, 12). The report of tris1,1,1,-5,5,5-hexafluoropentane-2,4-dionatorhenium(III), Re(HFAA)$_3$ (12), is undoubtedly correct. In fact, the method of preparation, of the tris complexes, used in this work was derived from that given for Re(HFAA)$_3$ (12). On the other hand, the compound described by Colton et al. (11a and b) as trispentane-2,4-dionatorhenium(III) bears no resemblance to the compound identified in this work as Re(AA)$_3$.

The Re(HFAA)$_3$ prepared from ReCℓ$_2$HFAA(PPh$_3$)$_2$ and NaHFAA has the same properties as that prepared by the method of Anderson and Brenner (12). Moreover, a structural determination using single crystal X-ray diffraction techniques is being performed (18). The two dimensional analysis of the structure indicates that the six oxygens in Re(HFAA)$_3$ form a nearly perfect octahedron around the central rhenium (18).

The compound described herein as Re(AA)$_3$ can be prepared in an analogous way to Re(HFAA)$_3$. Some difficulty was encountered in separating the product from contaminating triphenylphosphine and so a Re(IV) starting material was used instead of Re(III) as with Re(HFAA)$_3$. However, this problem has been overcome and Re(AA)$_3$ can be prepared from ReCℓ$_2$AA(PPh$_3$)$_2$; purification is accomplished by recrystallization from dry hexane (46).

The identities of Re(AA)$_3$ and Re(HFAA)$_3$ were further confirmed by analyses and molecular weight determinations using mass spectrometric methods. These data along with those for 'Colton's compound' and the previously reported $Re(HFAA)_3$ are given in TABLE 25.

It was stated earlier that 'Colton's compound' bears no resemblance to the compound described herein as $Re(AA)_3$. The physical properties of the two compounds are contrasted in TABLE 26.

Decomposition of $Re(AA)_3$ occurs in ether solution when care is not taken to exclude oxygen. The solution fades from a deep maroon to a bright red then reddish-brown and a brown solid precipitates. A few crystals of the bright red compound have been isolated and are being investigated (46). The brown solid can be crystallized from methylene chloride and petroleum ether to give dark yellow needles. The analysis and infrared spectrum of the compound are consistent with the formula $[Re(AA)_3]ReO_4$. Moreover, treatment of the compound with potassium chloride in methanol solution gives a different brown compound and potassium perrhenate (46). The compound, $[Re(AA)_3]ReO_4$, is quite different from 'Colton's compound' and it is unlikely that the very strong Re=O band in the infrared spectrum of $[Re(AA)_3]ReO_4$ would have been missed by Colton et al. (11a and b).

Attempts to duplicate the preparation of 'Colton's compound' have failed; only starting material and an intractable brown tar were obtained from the reaction as described (11a and b).

Although no suggestion can be made as to the identity of 'Colton's compound', further characterization of $Re(AA)_3$ and $Re(HFAA)_3$ has been accomplished. Molecular ions and complete fragmentation patterns have been recorded in the mass spectrometric investigation. Mass spectral data for $Re(AA)_3$ and $Re(HFAA)_3$ are given in TABLE 27.

TABLE 25

Analytical Data for Re(dik)$_3$ Compounds

Compound	% C		% H		% O		% Re		Molecular weight	
	calc	found	calc	found	calc	found	calc	found	calc	found
Re(AA)$_3$*	37.26	37.14	4.39	4.48	19.8		38.5		483,485	483,485
Re(HFAA)$_3$*	22.31	22.72	0.40	0.61	11.9		23.1		806,808	806,808
Colton's Compound$^+$	36.0	36.7	4.3	3.7	19.7	20.1	38.3	38.9	484	471
Re(HFAA)$_3$‡	22.3	22.0	0.4	0.7	-	-	23.1	22.4	-	-

* this work

\+ reference 11a and b (Calculations as per reference)

‡ reference 12

TABLE 26

Physical Properties of Re(AA)$_3$ and 'Colton's Compound'

Compound	Colour	Soluble in Ether	μ_{eff} at 25°C	μ_{eff}	χ_M
Re(AA)$_3$	maroon	yes	1.81 B.M.	$\mu_{eff} \alpha T^{1/2}$	constant
Colton's Compound	dark brown	no	2.33 B.M.	$\mu_{eff} \alpha T$	$\chi_M \alpha \frac{1}{T}$

A fluoride transfer from the HFAA ligand to rhenium in the case of $Re(HFAA)_3$ distinguishes the fragmentation pattern of this compound from that of $Re(AA)_3$. In fact, the $ReAAO_2H^+$ and $ReAAOH^+$ species found in the breakdown of $Re(AA)_3$ are not analogues of $ReHFAAO_2F^+$ or $ReHFAAOF^+$ but rather, they are hydroxyl-containing species similar to those found in the fragmentation schemes of $V(AA)_3$ and $Ti(AA)_3$ (47). Such a contrast in behaviour is not unexpected in view of the relative stability of Re-F bonds over Re-H bonds.

The fragment at m/e 398,396 has been identified in TABLE 27 as $ReO_2F_2(C_4HF_3O)^+$ but as noted, the formulae $ReOF_2(C_4HF_3O_2)^+$, $ReOF(C_4HF_4O_2)^+$ or $ReO_2F(C_4HF_4O)^+$ are possible. The formula $ReO_2F_2(C_4HF_3O)^+$ is considered the most reasonable because the fragment $(C_4F_3O)^+$ is relatively abundant, intensity 22, and can be derived from $C_4HF_3O^+$ by loss of H. That the HFAA fragment remaining on the rhenium in the m/e 398,396 species contains three fluorines instead of four is suggested by the fact that the CF_3^+ fragment is observed whereas CF_2^+ is not. Loss of $-CF_3$ by HFAA gives a species containing three fluorines. The $ReO_2F_2(C_4HF_3O)^+$ fragment would come from $ReHFAAOF_2^+$ by loss of $-CF_3$ and rupture of one of the C-O bonds in the ReHFAA chelate.

In the fragmentation pattern of $Cr(HFAA)_3$ both $-CF_2$ and $-CF_3$ losses are observed (48), whereas in the fragmentation of $Re(HFAA)_3$ only $-CF_3$ loss is observed. In addition, the transfer of -F from HFAA to the metal is not observed for $Cr(HFAA)_3$ (48).

Bancroft et al. (47) have suggested some pathways for the fragmentation of tris-acetylacetonates of first row transition metals. These are given in FIGURE 23. The major fragments in the breakdown of the tris-

TABLE 27

Mass Spectral Data for $Re(AA)_3$ and $Re(HFAA)_3$

$Re(AA)_3$			$Re(HFAA)_3$		
Fragment	m/e	Intensity	Fragment	m/e	Intensity
$Re(AA)_3^+$	484	94	$Re(HFAA)^+$	808	100
	482	56		806	60
			$Re(HFAA)_2(C_5HF_5O_2)^+$	789	36
				787	22
			$Re(HFAA)_2F_2^+$	639	<2
				637	<2
			$Re(HFAA)_2F^+$	620	54
				618	35
$Re(AA)_2O^+$	401	22	$Re(HFAA)_2O^+$	617	22
	399	14		615	13
$Re(AA)_2^+$	385	35	$Re(HFAA)_2^+$	601	4
	383	21		599	2
			$Re(HFAA)OF_2^+$	448	40
				446	25
			$Re(HFAA)F_2^+$	432	38
				430	25
			$Re(HFAA)OF^+$	429	34
				427	21
$Re(AA)O_2H^+$	319	13			
	317	10			
$Re(AA)O_2^+$	318	3			
	316	2			
			$Re(HFAA)F^+$	413	78
				411	48
$Re(AA)OH^+$	303	9			
	301	7			
$Re(AA)O^+$	302	17			
	300	11			
			$^*ReO_2F_2(C_4HF_3O)^+$	398	10
				396	6
$Re(AA)^+$	286	<2	$Re(HFAA)^+$	394	5
	284	<2		392	2
			$ReOF_2(C_4HF_3O)^+$	382	10
				380	6
			$ReO_2F(C_4HF_3O)^+$	379	9
				377	5
			$ReOF(C_4HF_3O)^+$	363	5
				361	3

* or $ReOF_2(C_4HF_3O_2)^+$ or $ReOF(C_4HF_4O_2)^+$ or $ReO_2F(C_4HF_4O)^+$

TABLE 27 continued

$Re(AA)_3$			$Re(HFAA)_3$		
Fragment	m/e	Intensity	Fragment	m/e	Intensity
			$ReO_2F_2^+$	257	36
				255	22
			$ReOF_2^+$	241	11
				239	8
			ReO_2F^+	238	<2
				236	<2
$Re(AA)_3^{2+}$	242	10	$Re(HFAA)_3^{2+}$	404	<2
	241	6		403	<2
			$C_5HF_6^+$	175	8
			$C_5HF_5O^+$	172	9
			$C_5HF_4O_2^+$	169	18
			$C_5HF_5^+$	156	4
			$C_5HF_4O^+$	153	22
			$C_4F_3O_2^+$	137	6
			$C_3F_3O_2^+$	125	50
			$C_4F_3O^+$	119	22
			$C_4F_3^+$	103	28
			$C_3F_3^+$	91	21
			CF_3^+	69	13

TABLE 28

Relative Intensities of Major Fragments in the Breakdown of Some $M(AA)_3$ Compounds

Fragment	Ti	V	Re	Cr	Mn
P^+ $M(AA)_3^+$	100	32	100	23	16
P-82 $MOH(AA)_2^+$	37	3	-	-	-
P-83 $MO(AA)_2^+$	-	-	22	-	-
P-99 $M(AA)_2^+$	55	100	35	100	100
P-114 $M(AA)(C_4H_4O_2)^+$	-	-	-	5	32
P-118 $MOH(C_5H_5O)_2^+$	12	-	-	-	-
P-124 $MOH(AA)(C_3H_5O)^+$	7	-	-	-	-
P-141 $M(AA)(C_3H_5O)$	-	-	-	-	6
P-164 $MO_2H_2(AA)^+$	7	-	-	-	-
P-165 $MO_2H(AA)^+$	-	7	14	-	-
P-180 $MOH_2(AA)^+$	16	-	-	-	-
P-181 $MOH(AA)^+$	36	10	10	12	-
P-182 $MO(AA)^+$	64	26	18	-	-
P-197 $MO(C_4H_4O_2)^+$	-	3	-	-	-

TABLE 28 continued

Fragment	Ti	V	Re	Cr	Mn
P-198 $M(AA)^+$	-	<5	<2	45	70
P-200 $MO(C_5H_5O)^+$	18	3	-	-	-
P-213 $M(C_4H_4O_2)^+$	-	-	-	4	3
P-216 $M(C_5H_5O)^+$	-	-	-	3	3
P-218*	17	-	-	-	-
P-281 MO^+	-	34	-	-	?
P-297 M^+	-	-	-	2	?

* Not identified

FIGURE 23

Suggested decomposition pathways for $M(AA)_3$ compounds. (Ref. 47)

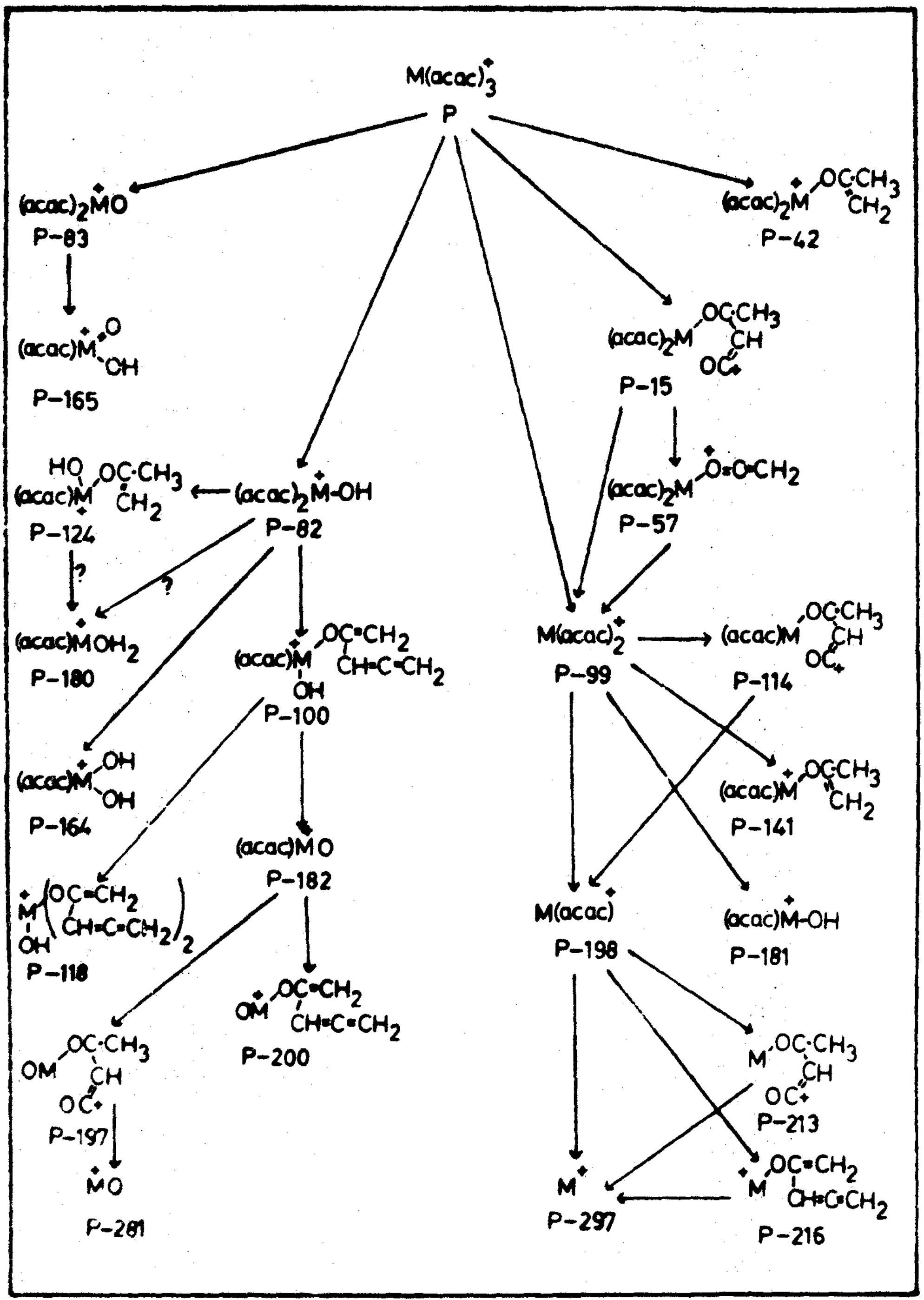

M(acac)3+
P
(acac)2MO+
P-83
(acac)M+ O OH
P-165
(acac)2M+ OC·CH3 CH2
P-42
(acac)2M OC·CH3 CH OC+
P-15
(acac)2M+ O=C=CH2
P-57
HO (acac)M+ OC·CH3 CH2
P-124
(acac)2M+-OH
P-82
?
?
(acac)M+OH2
P-180
(acac)M+ OC=CH2 CH=C=CH2 OH
P-100
M(acac)2+
P-99
(acac)M OC·CH3 CH OC+
P-114
(acac)M+ OH OH
P-164
(acac)M+O
P-182
(acac)M+ OC·CH3 CH2
P-141
M+ (OC=CH2 CH=C=CH2)2 OH
P-118
M(acac)+
P-198
(acac)M+-OH
P-181
OM OC·CH3 CH OC+
P-197
OM+ OC=CH2 CH=C=CH2
P-200
M OC·CH3 CH OC+
P-213
M+O
P-281
M+
P-297
M+ OC=CH2 CH=C=CH2
P-216

FIGURE: 23

acetylacetonates of Ti, V, Re, Cr and Mn are given in TABLE 28. It can be seen that the rhenium compound resembles the vanadium compound in its fragmentation pattern and is midway between the extremes of behaviour shown by $Ti(AA)_3$ and $Mn(AA)_3$.

Bancroft et al.(47) were "unable to find any simple correlation between the measured appearance potentials [of metal-containing fragments in the mass spectra of metal acetylacetonates] and a parameter relating to the complexed metal ions".

Holm and Cotton (49) were unable to correlate "any simple parameter of the complexed metal ion" with the ultraviolet-visible spectra they recorded for some thirty acetylacetonate complexes. They did state, however, that the energy of a particular transition (around 35,000 cm^{-1} and presumed to be π-π^*) was "determined by several parameters, among which is the ability of the metal ion to participate in $d\pi$-$p\pi$ overlap with the π system of the chelate ring" (49).

The electronic spectra of $Re(AA)_3$ and $Re(HFAA)_3$ show more bands than the spectra recorded by Holm and Cotton (49). The spectral data are given in TABLE 29.

Attempts to assign the observed bands to specific electronic transitions in the d^4 system (Re (III) has four 5d electrons) developed by Kamimura et al.(50) have failed. Such an interpretation would have totally ignored any $d\pi$-$p\pi$ overlap. The magnitudes of the extinction coefficients of the bands are more characteristic of absorptions arising from charge transfer processes than from d-d transitions. Thus no values for the ligand field parameter 10Dq or the spin-orbit coupling parameter ζ_{5d} are available from an interpretation of the electronic spectra of these

TABLE 29

Electronic Spectra of $Re(AA)_3$ and $Re(HFAA)_3$

$Re(AA)_3$	$Re(HFAA)_3$
38,900 cm^{-1}	37,300
$5.3x10^3$ ϵ_{max}	$6.6x10^3$
37,500	35,700
$5.7x10^3$	$6.5x10^3$
29,300	28,100
$3.1x10^3$	$4.7x10^3$
24,850	26,300
$3.2x10^3$	$4.5x10^3$
21,500	20,000
$1.6x10^3$	$4.5x10^3$
18,400	14,800
$2.1x10^3$	$5.4x10^3$
17,450	6,100
$2.2x10^3$	$4.3x10^2$
5,400	
$1.5x10^2$	

octahedral, spin-paired d^4 compounds.

An analysis of the magnetic susceptibility data for these compounds does give a value for the spin-orbit coupling parameter ζ_{5d}.

In CHAPTER 4, the prediction of the magnetic susceptibility value for d^4 systems made by Earnshaw et al. (41) was described. The susceptibilities of $Re(AA)_3$ and $Re(HFAA)_3$ are essentially temperature independent as predicted but don't quite reach the 1700×10^6 c.g.s.u. value predicted by Earnshaw (41). The magnetic data are given in TABLES 30 and 31. Variation in the magnetic susceptibility of $Re(AA)_3$ over the temperature range studied is less than 3%. For $Re(HFAA)_3$ the variation is less than 4%.

Figgis (51) gives a plot of μ_{eff} vs $kT/|\lambda|$ for the $^3T_{1(g)}$ ground term of spin-paired d^4 metal ions in octahedral environments. Values of $-2315\ cm^{-1}$ and $-2415\ cm^{-1}$ are obtained for $\lambda_{Re(III)}$ using the measured magnetic moments of $Re(AA)_3$ and $Re(HFAA)_3$ respectively. This gives a mean value of $4730\ cm^{-1}$ for ζ_{5d} ($\zeta_{5d} = -2\lambda$ for d^4) based on the measured magnetic moments of $Re(AA)_3$ and $Re(HFAA)_3$. Previous values given for ζ_{5d} are considerably lower. Earnshaw et al. (41) give $2500\ cm^{-1}$, and Eisenstein (35) gives $2300\ cm^{-1}$ for ζ_{5d}.

The discrepancy between the value calculated here and those reported earlier may lie in the use of an interpretation of magnetic behaviour based on a point charge model (51). As pointed out by Holm and Cotton (49) the situation in metal trisacetylacetonates probably involves $d\pi$-$p\pi$ overlap or charge transfer. However, as no theoretical treatment of magnetic susceptibility is available for more complex systems than those which approximate a point charge model, the calcu-

TABLE 30

Magnetic Susceptibility Data for Re(AA)$_3$

T°K	$10^6\chi_M$ c.g.s.u.	$\mu_{B.M.}$
83	1437	0.98
93	1430	1.04
104	1437	1.10
113	1437	1.14
124	1432	1.20
136	1432	1.25
151	1430	1.32
163	1437	1.37
177	1437	1.43
193	1430	1.49
209	1425	1.55
225	1421	1.61
241	1412	1.66
258	1405	1.71
273	1405	1.76
289	1402	1.81

TABLE 31

Magnetic Susceptibility Data for Re(HFAA)$_3$

T°K	$10^6\chi_M$ c.g.s.u.	$\mu_{B.M.}$
79	1337	0.92
95	1227	0.97
104	1210	1.01
113	1213	1.05
124	1227	1.11
137	1241	1.17
152	1256	1.24
164	1266	1.29
177	1273	1.35
193	1284	1.41
208	1284	1.47
225	1291	1.53
242	1294	1.59
258	1291	1.64
271	1291	1.68
290	1287	1.74

lation was made with the existing theory.

An empirical approach has also been used in the interpretation of infrared spectral data for these compounds. The spectra were recorded for the region 300 cm^{-1} to 2000 cm^{-1} and the absorption bands are tabulated in TABLE 32. The assignments given for bands above 700 cm^{-1} are those by Nakamoto (52) for $A\ell(AA)_3$ and by Morris et al. (53) for $A\ell(HFAA)_3$. "Nakamoto and co-workers have found that substitution of CF_3 for CH_3 causes marked shifts of the (C···C) and (C···O) stretching bands to higher frequencies and of the M-O stretching band to a lower frequency". This is obviously not the case for $Re(AA)_3$ and $Re(HFAA)_3$ in so far as the position of the (C···C) and (C···O) stretching bands are concerned. It might be expected then that the (M-O) stretching bands in the two compounds would by very similar if Nakamoto's (52) reasoning concerning a relationship between the strength of the (M-O) bond and the inductive effect of a CF_3 group is valid. Rhenium-oxygen bonds are much stronger than the first row transition metal-oxygen bonds with which Nakamoto (52) was concerned.

Bands at 459 cm^{-1} and 355 cm^{-1} in the spectrum of $Cr(AA)_3$ have been assigned by Gillard et al. (54) to MO_6 modes. The strong band at 395 cm^{-1} in the spectra of $Re(AA)_3$ and $Re(HFAA)_3$ is, by analogy, assigned to a (Re-O) stretch.

Other bands in the region below 700 cm^{-1} probably involve various ring deformations.

In TABLE 33, the infrared spectra of $Re(AA)_3$, $[Re(AA)_3]ReO_4$ and $ReC\ell_2(AA)_2$ are compared. It was seen earlier (Chapter 4) that the change in geometry from cis to trans in the $ReC\ell_2(AA)_2$ system made little or no

TABLE 32

Infrared Spectral Data for $M(dik)_3$ Compounds

$Re(AA)_3$	$A\ell(AA)_3$	Assignment	$Re(HFAA)_3$	$A\ell(HFAA)_3$	Assignment
1545sh.	1590	$\nu(C\underline{\cdots}C)$	1560s.	1654	$\nu(C\cdots C)$
1530sh.	$\left.\begin{matrix}1545\\1530\end{matrix}\right\}$	$\nu(C\underline{\cdots}O)$	1535m.	1636	$\nu(C\overline{\cdots}O)$
1545v.s.				1578	$\nu(C\underline{\cdots}O)+\delta(C\text{-}H)$
				1552	
	1466}	$\nu(C\underline{\cdots}O)+\delta(C\text{-}H)$		1483	
1420m.			1415v.s.	1452	
1380v.s.	1387	$\delta_d(CH_3)$			
1365v.s.	1387	$\delta_s(CH_3)$			
			1325v.s.	1370	$\nu(C\underline{\cdots}C)+\nu(C\text{-}F)$
1274	1288	$\nu(C\underline{\cdots}C)+\nu(C\text{-}CH_3)$			
			1267v.s.	1262	$\nu(C\text{-}F)$
			1225m.	1222	
			1205m.		
1190	1191	$\delta(C\text{-}H)$	1175sh.		
			1164m.	$\left.\begin{matrix}1162\\1150\end{matrix}\right\}$	$\delta(C\text{-}H)$
			1148m.		
			1105m.	1122	
				1048	
1022	1028	$\rho_\nu(CH_3)$			
			946m.		
935m.	935	$\nu(C\text{-}CH_3)+\nu(C\underline{\cdots}O)$			
910v.w.					
			830m	816	$\nu(C\text{-}CF_3)+\delta(C\text{-}H)$
780m.	$\left.\begin{matrix}788\\772\end{matrix}\right\}$	$\pi(C\text{-}H)$			
			750m	748	$\nu(C\text{-}CF_3)$
	685		686s.	672	

TABLE 32 continued

Infrared Spectral Data for M(dik)$_3$ Compounds

Re(AA)$_3$	Aℓ(AA)$_3$	Assignment	Re(HFAA)$_3$	Aℓ(HFAA)$_3$	Assignment
652m.	658				
620s.			608m.		
614sh.	594		590v.w.		
	577				
545v.w.					
	490	ν(H-O)			
444m.					
421sh.	425				
418m.	416		417m.		
411sh.					
395s.		ν(Re-O)	394s.		ν(Re-O)
316m.			314m.		
288v.w.					

difference in the infrared spectrum. It was anticipated that the infrared spectra of $Re(AA)_3$ and $[Re(AA)_3]ReO_4$ at least in the region characteristic of the acetylacetonate anion, would be nearly identical. Examination of TABLE 33 reveals that the spectrum of $[Re(AA)_3]ReO_4$ resembles that of trans-$ReC\ell_2(AA)_2$ more closely than it does the spectrum of $Re(AA)_3$. Not only is the acetylacetonate anion absorption region similar but also the strong absorption around 465 cm^{-1} assigned ν(Re-O) and the combination bands δ(C-H)+ν(Re-O) at 686 cm^{-1} and δring+ν (Re-O) at 610 cm^{-1}. Probably, the stereochemistries of $[Re(AA)_3]ReO_4$ and trans-$ReC\ell_2$ are completely different.

It is suggested that the infrared spectra of these compounds vary more with the oxidation state of the central metal than with the stereochemistry of the compound.

TABLE 33

Comparison of Infrared Spectra of Some Rhenium-acetylacetonate Complexes

$Re(AA)_3$	$[Re(AA)_3]ReO_4$	trans-$ReC\ell_2(AA)_2$
1545 sh.	1550 sh.	1535 v.s.
1530 sh.	1520 v.s.	
1515 v.s.	1510 sh.	
		1480 sh.
	1430 sh.	1440 sh.
1420 m.	1425 s.	1420 s.
1380 v.s.	1370 w.	1385 sh.
1365 s.	1360 w.	1375 s.
	1345 sh.	
	1330 w.	
	1320 m.	1318 s.
	1310 m.	1296 sh.
	1280 sh.	1287 s.
1274 s.		1193 w.
1190 m.		1189 sh.
	1040 s.	1031 s.
1022 m.	1020 sh.	1021 sh.
935 m.	952 s.	938 s.
910 v.w.	906 v.s.	
	900 sh.	
810 w.		812 s.
780 m.	784 s.	
		760 v.w.
		744 w.
	718 v.w.	720 v.w.
		698 sh.
	686 s.	686 s.
652 m.	650 v.w.	650 w.
620 s.		
614 sh.	610 s.	610 s.
		584 v.w.
		526 sh.
		520 w.
		510 w.
		501 sh.
		491 v.w.
	472 s.	464 s.
444 m.		
421 sh.		422 m.
418 m.	414 m.	
411 sh.		
395 s.		

TABLE 33 continued

$Re(AA)_3$	$[Re(AA)_3]ReO_4$	trans-$ReC\ell_2(AA)_2$
		309 v.s.
		386 sh.
		253 s.
		245 s.

CHAPTER 7

EXPERIMENTS

1. Physical Methods

1.1 Analyses

Elemental analyses and molecular weight determinations were performed by the following commercial laboratories, -

Galbraith Laboratories Inc., Knoxville, Tennessee
Imperial College Microanalytical Laboratory, London, England
A.B. Gygli, Toronto, Ontario
Alfred Bernhardt Mikroanalytisches Laboratorium

The neutron activation method for rhenium:chlorine ratios, developed in this laboratory (55) proved to be unsatisfactory for the triphenylphosphine-containing and hydrogen peroxide resistant complexes described in this work.

1.2 Infrared Spectra

Routine spectra were recorded on Perkin-Elmer Model 337 and Model 301 spectrometers. Solid samples were ground into a mull with nujol or fluorolube oil and mounted between potassium bromide or polyethylene plates. The mulling agents were vacuum distilled and stored over freshly regenerated molecular sieves (Linde Type 4A).

1.3 Ultraviolet and Visible Spectra

A Cary Model 14 spectrometer was used to record the ultraviolet and visible spectra. Solutions were studied in 1 cm. matched silica cells.

1.4 Magnetic Susceptibilities

Measurements of the magnetic susceptibilities of powdered, solid samples were made on a modification (56) of the Gouy apparatus designed by Earnshaw (57) and Newport Instruments (Bucks., England) (58). To minimize packing errors, the samples, in 3 mm. (o.d.) quartz tubes, were placed in the vibrator of a Hoover (Philadelphia, Pennsylvania) Unimelt melting-point apparatus and shaken to a constant 10 cm. length. Calibration of the apparatus was accomplished using mercury-thiocyanatocobaltate(II), obtained from Eastman Organic Chemicals, Rochester, New York.

Magnetic susceptibilities were measured at four different field strengths to check for ferromagnetic behaviour of either the sample or any impurities present. Corrections for diamagnetism of ligands and metal ions were taken from Selwood (59) and Foëx (60). These are given in the Appendix.

1.5 Mass Spectra

Members of Dr. D.B. Maclean's research group kindly recorded the mass spectra on a Consolidated Electrodynamics Corporation Analytical and Control Division Mass Spectrometer Model 21-110B.

1.6 X-ray Diffraction Patterns

X-ray diffraction pattern photographs of powdered samples were recorded on a Debye-Scherrer camera using CuKα radiation. The samples were sealed inside quartz Lindeman tubes. Line intensities were measured from the photographs with a Joyce-Loebl microdensitometer.

2. Solvents and Reagents

All solvents and reagents used were reagent grade. Solvents were dried when necessary by treatment with freshly regenerated molecular sieves (Linde Type 4A) and were de-oxygenated by bubbling dry nitrogen through them using a dispersion bubbler.

3. Preparation of Rhenium Compounds Used as Starting Materials

3.1 Oxomethoxodihalobistriphenylphosphinerhenium(V) - $ReO(OMe)X_2(PPh_3)_2$

These compounds were prepared by the method of Johnson et al. (20) using the appropriate hydrohalic acid. The compounds where recrystallized from mixtures of methylene chloride and acetone (or methanol), when necessary, to obtain the grey, trans isomer (21).

3.2 Nitridodichlorobistriphenylphosphinerhenium(V) - $ReNC\ell_2(PPh_3)_2$

This compound was prepared by the method of Johnson (27).

3.3 Pentachlororhenium(V) - $ReC\ell_5$

Rhenium heptoxide was reacted with carbon tetrachloride as described by Knox et al (61).

4. Preparation of Re(V) β-ketoenolate Complexes

4.1 Oxodichloropentane-2,4-dionatotriphenylphosphinerhenium(V) - $ReOC\ell_2AAPPh_3$

One millilitre of 2,4-pentanedione (acetylacetone) was added to a well-stirred suspension of one gram of grey $ReO(OMe)C\ell_2(PPh_3)_2$ in 200 ml. of acetone. The mixture was warmed gently until all the $ReO(OMe)C\ell_2(PPh_3)_2$ had disappeared (about 45 minutes). The resulting, green solution was evaporated to a small volume (about 10 ml.) using a rotary evaporator.

Fifty millilitres of methanol were added and a green solid precipitated. The green solid was redissolved in acetone and any unreacted $ReO(OMe)C\ell_2(PPh_3)_2$ was removed by filtration. The addition of methanol to the filtrate gave emerald green platelets which were isolated by filtration and washed with several portions of ethyl ether. Yield .57 grams (75%) [Found C 43.87, H 3.58, P 5.08, Cℓ 11.41%; $C_{23}H_{22}C\ell_2PO_3Re$ requires C 43.54, H 3.49, P 4.94, Cℓ 11.17%].

If the starting material $ReO(OMe)C\ell_2(PPh_3)_2$ was a mixture of isomers and not just the grey, trans isomer, two additional isomers of $ReOC\ell_2AAPPh_3$ were obtained, one lime green and the other blue. In addition, a fourth isomer, dark green, was isolated on one occasion from a solution of the other three that had been treated with a little acetylacetone in refluxing benzene for about 18 hours.

Analyses for three of the isomers of $ReOC\ell_2AAPPh_3$ are given in TABLE 34.

Analogues of $ReOC\ell_2AAPPh_3$ were prepared using 1-phenyl-1,3-butanedione* and 1,3-diphenyl-1,3-propanedione*. Fluoro substituted β-diketones such as 1,1,1-5,5,5-hexafluoropentane-2,4-dione (hexafluoroacetylacetone) did not give products of this type.

4.2 Nitridochloro-1,1,1-5,5,5-hexafluoropentane-2,4-dionatobistriphenylphosphinerhenium(V) - $ReNC\ell HFAA(PPh_3)_2$

One gram of $ReNC\ell_2(PPh_3)_2$ and 1 g of sodium hexafluoroacetylacetonate were refluxed 4 hours in 100 ml. of a 9:1 (by volume) benzene-acetone mixture under an atmosphere of nitrogen. The solution was evaporated to

---

* see Appendix for analyses

TABLE 34

Analytical Data for $ReOC\ell_2AAPPh_3$ Isomers

Calculated %		Found		
		lime green	emerald green	blue
C	43.53	44.15	43.87	43.34
H	3.49	3.90	3.58	3.47
P	4.94			
Cℓ	11.17	11.13	11.41	10.67

TABLE 35

Analytical Data for $ReX_2(AA)_2$ Compounds

Compound	% C		% H		% X	
	found	calc.	found	calc.	found	calc.
trans-$ReC\ell_2(AA)_2$	26.35	26.38	3.07	3.10	15.26	15.57
cis-$ReC\ell_2(AA)_2$	27.20	26.38	3.08	3.10	15.93	15.57
$ReBr_2(AA)_2$	21.64	22.06	2.76	2.59	30.62	29.36
$ReI_2(AA)_2$	18.88	18.82	2.55	2.21	38.42	39.76

a small volume (about 10 ml.) on a rotary evaporator and the compound precipitated with an excess of methanol. Dark red needles were obtained by treating a methylene chloride solution of the compound with methanol. Yield 80% (estimated) [Found C 51.03, H 3.26, P 6.23 N 1.34, Cℓ 3.62% (fluorine analysis not yet received from Imperial College); $C_{41}H_{31}F_6C\ell NP_2O_2Re$ requires C 51.0, H 3.24, P 6.43, N 1.48, Cℓ 3.67%].

Attempts to prepare the acetylacetonate analogue of this compound in quantity were unsuccessful.

5. Preparation of Re(IV) β-ketoenolate Complexes

5.1 Trichloro-1-phenyl-1,3-butanedionatotriphenylphosphinerhenium(IV) - $ReC\ell_3BAPPh_3$

On one occasion a compound with the stoichiometry $ReC\ell_3BAPPh_3$ was isolated from the reaction between $ReO(OMe)C\ell_2(PPh_3)_2$ and 3-mercapto-1-phenylbut-2-en-1-one, (monothiobenzoylacetone).

One gram of monothiobenzoylacetone and 3 g of $ReO(OMe)C\ell_2(PPh_3)_2$ were refluxed in 200 ml. acetone for about 100 hours under an atmosphere of nitrogen. The red solution produced was evaporated to a small volume (about 10 ml.) on a rotary evaporator and treated with methanol to precipitate the compound. Red crystals were obtained from a methylene chloride-methanol mixture. Yield 20% (estimated). [Found C 47.28, H 3.59, Cℓ 14.76, P 4.57% molecular weight 698; $C_{46}H_{39}C\ell_3P_2O_2Re$ requires C 46.9, H 3.38, Cℓ 14.85, P 4.31% molecular weight 716].

When the reaction was tried with 4-mercaptopent-3-en-2-one (monothioacetylacetone), no rhenium-containing compound could be isolated. However, triphenylphosphine sulphide was isolated from the reaction mixture.

5.2 Dihalobispentane-2,4-dionatorhenium(IV) - $\mathrm{ReX_2(AA)_2}$

These compounds were usually prepared by the method of Grove et al. (4), using the appropriate chloro, bromo or iodo $\mathrm{ReO(OMe)X_2(PPh_3)_2}$ starting material.

From the combined filtrates of several preparations of $\mathrm{ReC\ell_2(AA)_2}$, a small amount (∿ 200 mg) of a brown, crystalline compound was isolated. This was shown to be cis-$\mathrm{ReC\ell_2(AA)_2}$. Analytical data for this compound and the other $\mathrm{ReX_2(AA)_2}$ compounds are given in TABLE 35.

5.3 Dichlorobispentane-2,4-dionatorhenium(IV) - $\mathrm{ReC\ell_2(AA)_2}$

$\mathrm{ReOC\ell_2AAPPh_3}$ (.6 g) was refluxed in 5 ml. acetylacetone for 4 hours under an atmosphere of nitrogen. The solution was cooled and the orange crystals collected by filtering the solution. Yield .25 g (58%).

This compound could also be prepared by treating $\mathrm{ReC\ell_2AA(PPh_3)_2}$ and/or $\mathrm{ReC\ell_2AAOPPh_3PPh_3}$ with acetylacetone under reflux conditions.

6. Preparation of Re(III) β-ketoenolate Complexes

6.1 Dihalo-β-diketonatobistriphenylphosphinerhenium(III) - $\mathrm{ReX_2dik(PPh_3)_2}$

An extensive series of these compounds has been prepared by the method of Grove et al. (4).

Analytical data for the compounds prepared are given in TABLE 36.

6.2 Dichloropentane-2,4-dionatotriphenylphosphineoxidetriphenylphosphinerhenium(III) - $\mathrm{ReC\ell_2AAOPPh_3PPh_3}$

Two grams of $\mathrm{ReO(OMe)C\ell_2(PPh_3)_2}$ were refluxed in 50 ml. acetone containing 2 ml. acetylacetone, for 4 hours under an atmosphere of nitrogen. The resulting, red solution was concentrated and treated with methanol to precipitate the $\mathrm{ReOC\ell_2AAPPh_3}$ left (about .2 g). Treatment

TABLE 36

Analytical Data for $ReX_2dik(PPh_3)_2$ Compounds

Compound	% C		% H		% X		Molecular Weight	
	found	calc.	found	calc.	found	calc.	found	calc.
$ReC\ell_2AA(PPh_3)_2$		55.91		4.23		8.05		880.8
$ReBr_2AA(PPh_3)_2$	50.36	50.78	4.09	3.83	16.48	16.48	708	969.7
$ReI_2AA(PPh_3)_2$	46.35	46.29	3.81	3.51	23.67	23.86	-	1063.7
$ReC\ell_2DBM(PPh_3)_2$	60.98	60.95	4.31	4.11	7.88	7.06	-	1004.9
$ReBr_2DBM(PPh_3)_2$	55.75	56.00	3.86	3.78	14.69	14.61	-	1093.8
$ReI_2DBM(PPh_3)_2$	52.21	51.57	3.72	3.48	22.17	21.37	-	1187.8
$ReC\ell_2HFAA(PPh_3)_2$	48.88	49.80	3.17	3.16	7.17	7.17	-	988.7
$ReBr_2HFAA(PPh_3)_2$	44.47	45.69	2.42	2.90	11.57	14.83	-	1077.7
$ReI_2HFAA(PPh_3)_2$	41.99	42.03	2.50	2.67	25.94	21.66	-	1171.6
$ReC\ell_2BA(PPh_3)_2$	58.87	58.59	4.44	4.17	7.37	7.52	782	942.9
$ReBr_2BA(PPh_3)_2$	53.31	53.54	3.82	3.81	15.92	15.49	-	1031.8
$ReI_2BA(PPh_3)_2$	51.08	49.08	3.94	3.49	22.51	22.55	-	1125.7
$ReC\ell_2EBA(PPh_3)_2$	58.05	58.02	4.27	4.25	7.75	7.29	-	972.9
$ReBr_2EBA(PPh_3)_2$	53.05	53.16	3.74	3.89	15.61	15.05	1022	1061.8
$ReI_2EBA(PPh_3)_2$	48.78	48.84	3.47	3.58	23.00	21.96	-	1155.8
$ReC\ell_2EAA(PPh_3)_2$	54.26	55.38	3.99	4.32	8.53	7.79	-	910.8
$ReBr_2EAA(PPh_3)_2$	50.46	48.65	4.14	3.93	16.97	15.99	-	999.7
$ReI_2EAA(PPh_3)_2$	45.47	46.12	3.88	3.59	24.04	23.21	1030	1093.7
$ReC\ell_2TFTA(PPh_3)_2$	52.16	52.69	3.54	3.42	6.97	7.07	994	1002.9
$ReBr_2TFTA(PPh_3)_2$	48.89	48.40	3.16	3.14	15.31	14.64	-	1091.8
$ReI_2TFTA(PPh_3)_2$	42.44	44.57	2.57	2.89	21.56	21.40	-	1185.7
$ReC\ell_2TFBA(PPh_3)_2$	55.43	55.42	3.84	3.64	8.03	7.11	-	996.8

TABLE 36 continued

Compound	% C		% H		% X		Molecular Weight	
	found	calc.	found	calc.	found	calc.	found	calc.
$ReBr_2TFBA(PPh_3)_2$	52.88	50.88	3.76	3.34	15.44	14.72	1037	1085.8
$ReI_2TFBA(PPh_3)_2$	47.25	46.83	3.27	3.08	24.43	21.51	-	1179.7

of the filtrate with ether and petroleum ether (B.p. 30°-60°C) gave red crystals which were recrystallized from a mixture of methylene chloride and petroleum ether. Yield 1.3 g (67%). [Found C 54.76, H 4.35, P 6.96, Cℓ 8.83%; $C_{41}H_{37}C\ell_2P_2O_3Re$ requires C 54.9, H 4.17, P 6.92, Cℓ 7.92%. Oxygen analysis has not yet been received from Imperial College.]

This compound was also prepared by reacting $ReOC\ell_2AAPPh_3$ with molten triphenylphosphine. Moreover, if the green solution of $ReOC\ell_2AAPPh_3$ and triphenylphosphine, obtained from the reaction described in 4.1, was refluxed for 4 hours under nitrogen, $ReC\ell_2AAOPPh_3PPh_3$ was obtained. In fact, this product was first isolated from the combined filtrates of several preparations of $ReOC\ell_2AAPPh_3$.

If the reaction of acetylacetone with $ReO(OMe)C\ell_2(PPh_3)_2$ to give $ReC\ell_2(AA)_2$ (5.2) was stopped after about one hour, very large crystals of $ReC\ell_2AAOPPh_3PPh_3$ were obtained.

When all of the isolable products of the reaction between $ReO(OMe)C\ell_2(PPh_3)_2$ and acetylacetone in benzene solution (preparation of $ReC\ell_2AA(PPh_3)_2$, 6.1) were examined in detail, some $ReC\ell_2AAOPPh_3PPh_3$ was isolated.

6.3 Dichloropentane-2,4-dionatodiphenylmethylphosphineoxidetriphenylphosphinerhenium(III) - $ReC\ell_2AAOPPh_2MePPh_3$

A 1:1 mole ratio mixture of diphenylmethylphosphine (.15 g) and $ReOC\ell_2AAPPh_3$ (.48 g) were refluxed in 50 ml. acetone for 6 hours under an atmosphere of nitrogen. The reaction mixture was cooled and addition of an excess of petroleum ether (B.p. 30°-60°C) gave an orange precipitate. Attempts to obtain a crystalline sample for analysis were unsuccessful.

The P-sensitive bands of the infrared spectrum of this compound were very much different from those in the spectrum of $ReC\ell_2AAOPPh_3PPh_3$. Attempts to obtain a proton magnetic resonance spectrum of the compound failed.

The compound (∿ .3 g) was refluxed in 5 ml. dry pyridine for four hours under nitrogen. Two pyridine-containing products were isolated, - ReO_2py_4 and $ReC\ell_2AApyPPh_3$. These were identified by comparison with authentic samples of these compounds. The pyridine solution of the reaction mixture was treated with petroleum ether to precipitate any rhenium-containing compounds. The filtrate was concentrated and placed in an evacuated chamber to remove the remaining pyridine. The proton magnetic resonance spectrum of a deuterochloroform solution of the residue showed a doublet at 114 and 127 Hz. (Spectrum recorded on a Varian Model T-60 spectrometer). This was identified as the methyl resonance of the compound $OPPh_2Me$ by comparison with an authentic spectrum of this compound furnished by W. Louch.

It was concluded that the phosphine oxide portion of the complex had been diphenylmethylphosphine oxide and that the complex was $ReC\ell_2AAOPPh_2MePPh_3$.

6.4 Dichloropentane-2,4-dionatopyridinetriphenylphosphinerhenium(III) - $ReC\ell_2AApyPPh_3$

One half gram of $ReC\ell_2AAOPPh_3PPh_3$ was refluxed in 15 ml. dry pyridine for 4 hours under nitrogen. The solution was cooled and the reddish-orange crystals were isolated by filtration. Yield ∿ 60% (estimated). [Found C 49.20, H 3.94, P 4.54, N 2.05, Cℓ 10.38%; $C_{29}H_{27}C\ell_2NPO_2Re$ requires C 49.93, H 3.90, P 4.44, N 2.01, Cℓ 10.17%].

The compound could also be prepared from $ReC\ell_2AA(PPh_3)_2$.

6.5 Tris-1,1,1-5,5,5-hexafluoropentane-2,4-dionatorhenium(III) - $Re(HFAA)_3$

The preparation of $Re(HFAA)_3$ described by Anderson and Brenner (12) was modified through the use of $ReC\ell_2HFAA(PPh_3)_2$ instead of $Re_3C\ell_9$. The compound $ReC\ell_2HFAA(PPh_3)_2$ can be prepared in much higher yield (based on rhenium metal) than can $Re_3C\ell_9$.

In a typical experiment, 4 g of a 1:1 mixture (by weight) of finely powdered NaHFAA and $ReC\ell_2(HFAA)(PPh_3)_2$ were destructively distilled in a vacuum sublimation apparatus that was equipped with a cold finger. The reaction was allowed to proceed at about 200°C for 12 hours, after which the purple, crystalline product was scraped from the cold finger. Recrystallization from petroleum ether gave purple needles. Yield 60% (estimated). [Found C 22.72, H 0.61%; $C_{15}H_3F_{18}O_6Re$ requires C 22.31, H 0.40%].

6.6 Trispentane-2,4-dionatorhenium(III) - $Re(AA)_3$

Three grams of a 2:1 mixture (by weight) of finely powdered NaAA and $ReC\ell_2(AA)_2$ were placed in the apparatus shown in FIGURE 24. The system was evacuated and the oil bath heated to 215°C. The reaction was allowed to proceed for 24 hours. After removing the oil bath, the apparatus was cooled and sealed off at A. The dark, red crystalline solid was scraped from the sides of the glass tube and used without further purification. The compound seems to be stable in dry air but was handled in a nitrogen filled dry-box. Yield 30% (estimated). [Found C 37.14, H 4.48, $C_{15}H_{21}O_6Re$ requires C 37.26, H 4.39%].

When the compound was prepared from $ReC\ell_2AA(PPh_3)_2$ instead of $ReC\ell_2(AA)_2$, a product that was contaminated with triphenylphosphine was obtained. Early efforts to recrystallize the compound from ether-

FIGURE 24

Apparatus for the production of $Re(AA)_3$

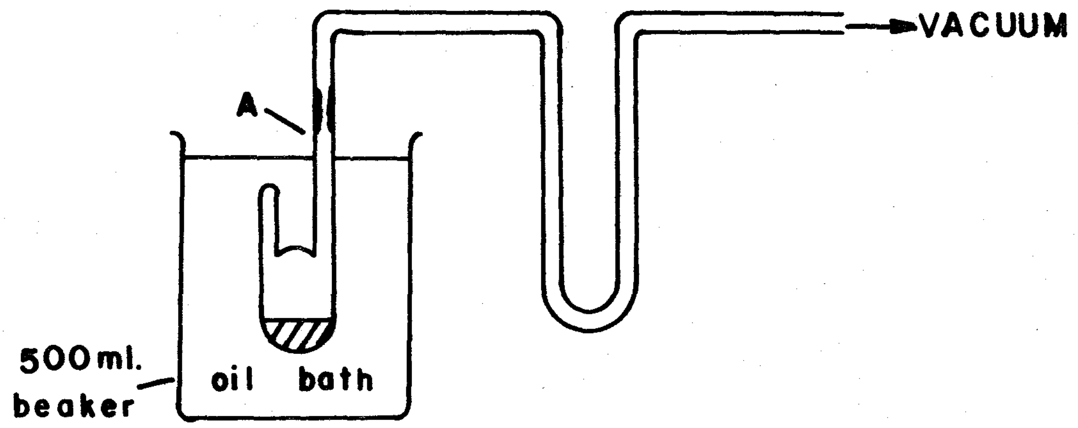


FIGURE 24

petroleum ether mixtures resulted in its decomposition. Recently (46), however, the compound has been recrystallized from an ether-hexane mixture.

7. The Oxidation of $Re(AA)_3$ in Ether Solution

As noted above, decomposition of $Re(AA)_3$ occurred in ether solution. The maroon solution faded to bright red and then to reddish-brown whereupon a brown solid precipitated. This solid was dissolved in methylene chloride and treatment of the solution gave yellow needles. These were identified (Chapter 6) as $[Re(AA)_3]ReO_4$. [Found C 25.01, H 3.17%; $C_{15}H_{21}O_{10}Re_2$ requires C 24.7, H 2.80%].

8. The Reaction of $ReO(OMe)C\ell_2(PPh_3)_2$ and Acetylacetone in Benzene

Two grams of $ReO(OMe)C\ell_2(PPh_3)_2$ were refluxed in 30 ml. benzene containing 2 ml. acetylacetone for 6 hours under an atmosphere of nitrogen as described by Grove et al. (4). The solution was concentrated and treated with methanol. This precipitated $ReC\ell_2AA(PPh_3)_2$ which was washed with acetone and then recrystallized from methylene chloride and methanol to give .9 g of orange plates. Yield 43%.

The filtrate and acetone washings were concentrated and treated with methanol to precipitate $ReOC\ell_2AAPPh_3$ which was removed by filtration and recrystallized from acetone-methanol to give .45 g green leaf-like crystals. Yield 30%. A small amount of $ReC\ell_2AAOPPh_3PPh_3$ was isolated from the $ReOC\ell_2AAPPh_3$ filtrate.

9. The Reaction of $ReOC\ell_3(PPh_3)_2$ with Granulated Zinc

One gram of $ReOC\ell_3(PPh_3)_2$ was stirred with 1 g granulated zinc in 200 ml. chloroform for 1/2 hour. The resulting, reddish-brown solution was concentrated to 50 ml. and treated with an excess of methanol. The grey, pearlescent precipitate produced was isolated by filtration and washed with several small portions of ether. A nearly qualitative yield (98%) of $ReO(OMe)C\ell_2(PPh_3)_2$ was obtained. [Found C 53.64, H 4.12, C $C\ell$ 8.70, P 7.91%; $C_{37}H_{33}C\ell_2P_2O_2Re$ requires C 53.8, H 4.03, $C\ell$ 8.58, P 7.49%].

The grey isomer of $ReO(OMe)C\ell_2(PPh_3)_2$ has been identified as the trans isomer (21). Thus, treatment with zinc seems to be a good way to test for or remove a chloride trans to a Re=O group.

10. The Reaction of $ReX_2(AA)_2$ with Halide Acceptors

It was noted that the residues from $Re(AA)_3$ preparations gave dark, blue-green solutions in methanol or acetone. This colour could be duplicated by reacting $ReX_2(AA)_2$ or $ReC\ell_2AA(PPh_3)_2$ with different halide acceptors; Na^+ from either NaAA or NaOMe and powdered zinc. No solid compound could be isolated from these reactions but the colour is very similar to that observed in the laboratory for solutions of $Re_2C\ell_8^{2-}$ or derivatives of this ion (56).

A green, unstable compound was isolated from the residues from $Re(HFAA)_3$ preparations. The infrared spectrum of the compound showed no bands characteristic of triphenylphosphine. It is suggested that the coloured solutions observed are characteristic of derivatives of $Re_2C\ell_8{}^{2-}$. Such compounds could result from halide abstraction from the $C\ell$-Re-$C\ell$ system and subsequent formation of Re-Re bonds between the resulting fragments.

Though the evidence is scant for this suggestion, the possibility of such simple access to these compounds is worthy of further investigation.

CHAPTER 8

CONCLUSIONS

1. Reaction Scheme

A reaction scheme has been developed which explains the formation of the products $ReOC\ell_2AAPPh_3$, $ReC\ell_2AAOPPh_3$, $ReC\ell_2AA(PPh_3)_2$ and $ReC\ell_2(AA)_2$ in the reaction between $ReO(OMe)C\ell_2(PPh_3)_2$ and acetylacetone. This scheme probably also applies to reactions of other β-ketoenols with $ReO(OMe)C\ell_2(PPh_3)_2$. In the case of fluoro-substituted β-ketoenols such as hexafluoroacetylacetone, however, compounds of the type $ReOC\ell_2dikPPh_3$ and $ReC\ell_2(dik)_2$ have not been isolated. It is likely that compounds such as $ReOC\ell_2HFAAPPh_3$ are extremely reactive and rapid conversion to $ReC\ell_2HFAA(PPh_3)_2$ occurs*. Once formed, $ReC\ell_2HFAA(PPh_3)_2$ is probably as resistant to oxidation as $Re(HFAA)_3$ is observed to be. In contrast, $ReC\ell_2AA(PPh_3)_2$ can be oxidized to give $ReC\ell_2(AA)_2$ and $Re(AA)_3$ is very easily oxidized.

2. Re(V) Compounds

In addition to the established emerald green isomer of $ReOC\ell_2AAPPh_3$ (Fig. 3), two other isomers have been isolated, one lime green, the other

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* Production of $ReC\ell_2HFAA(PPh_3)_2$ from $ReO(OMe)C\ell_2(PPh_3)_2$ and hexafluoroacetylacetone takes fifteen minutes; production of the AA analogue takes up to six hours.

blue. The dark green compound described in Chapter 2 is probably the remaining isomer as suggested, but not enough of the compound has been prepared to establish it unequivocally.

The remaining Re(V) compound described in Chapter 2 is the first nitrido-rhenium complex to be made with an oxygen-containing ligand. This compound, $ReNC\ell HFAA(PPh_3)_2$ reacts further with NaHFAA. The product of this reaction, though not obtained in pure form, is probably $ReN(HFAA)_2$. Such a compound might be used as a precursor to the nitrido analogues of the oxochlorides studied in this laboratory (56).

A crystallographic examination of the new isomers of $ReOC\ell_2AAPPh_3$ and of $ReNC\ell HFAA(PPh_3)_2$ might yield more information as to the nature of the short O-P distance in the $ReOC\ell_2AAPPh_3$ isomer already studied (17).

3. Re(IV) Compounds

No evidence for dimers of the type $Re_2C\ell_4(AA)_4$ (4) has been encountered in this investigation. However, both cis and trans forms of $ReC\ell_2(AA)_2$ monomer have been isolated from the reaction described by Grove et al. (4).

4. Re(III) Compounds

4.1 ReX_2dikL_2 Compounds

The most characteristic compounds produced by reacting β-ketoenols with $ReO(OMe)X_2(PPh_3)_2$ are those of the type $ReX_2(dik)(PPh_3)_2$.

Two new members of the general class of Re(III) compounds, ReX_2dikL_2, have been prepared $ReC\ell_2AAOPPh_3PPh_3$ and $ReC\ell_2AApyPPh_3$. The latter compound is the first reported pyridine-containing β-ketoenolate complex of rhenium. Further reaction of $ReC\ell_2AApyPPh_3$ with pyridine gives ReO_2py_4

and probably some $ReC\ell_2AA(py)_2$.

4.2 Trisβ-ketoenolate Complexes of Rhenium

Both $Re(HFAA)_3$ and $Re(AA)_3$ have been prepared and characterized. Previous reports of $Re(AA)_3$ (11a and b) are incorrect. It is possible, considering the facile oxidation of $Re(AA)_3$ by atmospheric oxygen, that the sample prepared by Colton (11a and b) contained some oxidation products of $Re(AA)_3$. That sample was neither $Re(AA)_3$ nor the oxidation product $[Re(AA)_3]ReO_4$, encountered in this work.

The isolation of $Re(AA)_3$ and $[Re(AA)_3)]ReO_4$ creates the possibility of preparing rhenium β-ketoenolate complexes with coordination numbers greater than 6.

The compound $[Re(AA)_3]ReO_4$ can probably be converted to $[Re(AA)_3]C\ell$ (46). If this compound is truly a 7-coordinate species, then further reaction with AA might be expected to give $Re(AA)_4$. The tetrakis complexes $M(AA)_4$ of titanium, zirconium and hafnium are prepared from the $MC\ell(AA)_3$ compounds in this fashion (29,30).

An investigation of higher coordination numbers in the rhenium-β-ketoenolate system is considered to be the most interesting extension of this work.

APPENDIX

1. Abbreviations used in the text.

1.1 Ligands

L	monodentate ligand
dik	β-diketonate anion
AA	2,4-pentanedionate anion
HFAA	1,1,1,5,5,5-hexafluoro-2,4-pentanedionate anion
DBM	1,3-diphenyl-1,3-propanedionate anion
BA	1-phenyl-1,3-butanedionate anion
TFAA	1,1,1-trifluoro-2,4-pentanedionate anion
TFTA	1,1,1-trifluoro-4-thienyl-2,4-butanedionate anion
TFBA	1,1,1-trifluoro-4-phenyl-2,4-butanedionate anion
EAA	1-ethoxy-1,3-butanedionate anion
EBA	1-ethoxy-3-phenyl-1,3-propanedionate anion
dipy	α,α'-dipyridyl
py	pyridine
Me	methyl
Et	ethyl
Ph	phenyl

1.2 Other

ν	stretching mode (infrared)
δ	bending mode (infrared)
ρ	rocking mode (infrared)
ε_{max}	maximum extinction coefficient

d	crystal lattice interplanar spacing
I	intensity
μ_{eff}	effective magnetic moment (corrected by inclusion of Weiss constant in calculation)
B.M.	Bohr magneton (units for μ_{eff})
s	strong (intensity of infrared bands)
sh	shoulder (with respect to unresolved infrared bands)
v.s.	very strong (intensity of infrared bands)
m.	medium "
w.	weak "
v.w.	very weak "
e.V.	electron volts
K.V.	kilo volts
m/e	mass to charge ratio (mass spectrometry)
X_M	molar magnetic susceptibility
X	magnetic susceptibility
θ	Weiss constant from Curie-Weiss law
ζ_{5d}	spin-orbit coupling parameter for a 5d electron
$10D_q$	ligand field splitting
c.g.s.u.	units of magnetic susceptibility in the centimeter-gram system
κ	orbital reduction factor
k	Boltzman constant
3B+C	Racah parameters
λ	spin-orbit coupling parameter for a term
ml.	millilitres
g	grams

cm^{-1} wavenumbers

2. Analytical data for $ReOC\ell_2dikPPh_3$ compounds

$ReOC\ell_2DBMPPh_3$ [Found: C, 52.62; H, 3.72; Cℓ, 8.86%; $C_{33}H_{26}C\ell_2PO_3Re$ requires C, 52.2; H, 3.43; Cℓ, 9.37%]

$ReOC\ell_2BAPPh_3$ [Found: C, 48.24; H, 3.52; Cℓ, 10.54%; $C_{28}H_{21}C\ell_2PO_3Re$ requires C, 48.3; H, 3.45; Cℓ, 10.2%].

3. Diamagnetic Corrections

AA - 54.9 c.g.s.u.
HFAA - 75.1 "
DBM - 129.5 "
BA - 92.2 "
TFAA - 65.0 "
TFTA - 99.9 "
TFBA - 102.3 "
EAA - 70.1 "
EBA - 107.4 "

$C\ell^-$ - 26.0 c.g.s.u.
Br^- - 36.0 "
I^- - 52.0 "
PPh_3 - 116.8 "
$OPPh_3$ - 122.4 "
py - 49.3 "
Re(III) - 36 "
Re(IV) - 28 "

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