

6-DIKETONE-CARBONYL COMPLEXES OF RHENIUM(I)

β -DIKETONE-CARBONYL COMPLEXES OF RHENIUM(I)

By

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...to Yolande, Louise and Julie

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SCOPE AND CONTENTS:

The reaction between chloropentacarbonylrhenium(I) and β -diketones is shown to give two types of products, $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{dik})_2$ and $\text{Re}_2(\text{CO})_6(\text{dik})_2$. A unique structure could not be established for either type using infra-red, nmr, mass spectrometry and magnetic measurements. Thus, a crystal structure of one member from each series was undertaken to solve the problem.

$\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{bamH})_2$: the two halves of the molecule are related by a two fold axis and are held together by chlorine bridges. The neutral β -ketoenol groups are cis to the chlorine bridges, are both on the same side of the molecule, and are each bonded to the rhenium atom via only one oxygen.

$\text{Re}_2(\text{CO})_6(\text{dbm})_2$: the two halves of the molecule are related by an inversion centre and are held together by one bridging oxygen from each β -diketone group. The angle between the O-Re-O plane and the OCCCCO β -diketone plane is 37° , the largest ever observed for a metal β -diketonate.

The $\text{Re}_2(\text{CO})_6(\text{dik})_2$ series was shown to undergo bridge breaking and further substitution to give products of the type $\text{Re}(\text{CO})_3(\text{dik})\text{L}$ and

and $\text{Re}(\text{CO})_2(\text{dik})\text{L}_2$ where $\text{L} = \text{CO}, \text{py}, \text{Ph}_3\text{P}$.

Finally, the crystal structure of an impurity, $\text{Re}_2\text{Cl}_4(\text{CO})_x$, was partially solved.

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Bond Distances and Angles in $\text{Re}_2\text{Cl}_4(\text{CO})_x$?

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CHAPTER I
INTRODUCTION

The preparation and some of the physical properties of tris(pentane-2,4-dionato)rhenium (III), $\text{Re}(\text{acac})_3^*$ described in the literature by Colton et al. (2,3). Workers in our laboratory have attempted, on many occasions, to make $\text{Re}(\text{acac})_3$ by the original method, the reaction of acetylacetone and ReO_2 and Re_2O_3 , but without success. Interest in $\text{Re}(\text{acac})_3$ stems from two reasons. First, the magnetic moment reported by Colton et al. is quite high ($\mu_{298} = 2.33$ B.M.) and the magnetic susceptibility varies markedly with temperature ($\chi_m \propto 1/(T+B)^{-1}$). This is unusual behaviour for a d^4 system in a heavy transition metal since it is expected that the susceptibility (χ_m) should be temperature independent (63). The results of Colton et al. are also quite unlike the magnetic behaviour of other monomeric $\text{Re}(\text{III})$ compounds (64). Secondly, $\text{Mn}(\text{acac})_3$, which might be expected to have analogous properties to $\text{Re}(\text{acac})_3$ has a structure which is markedly distorted from the D_3 symmetry expected for $\text{M}(\text{acac})_3$ compounds, and this distortion has been ascribed to the Jahn-

* acac is the anion of 2,4 pentanedione, $\text{C}_5\text{H}_7\text{O}_2^-$. For a complete list of abbreviations see Appendix C.

Teller effect (7). Spin orbit coupling, which is generally much larger for third row transition metals than for first row transition metals (63), should remove the ground state degeneracy of Re(III) and thus there should be no Jahn-Teller distortion. Thus, one might expect the structure of $Re(acac)_3$ to have nearly D_3 symmetry.

All attempts to prepare $Re(acac)_3$, before this work was started, had used either Colton's method or started from compounds of Re(III), Re(IV) or Re(V) (24). Since it had proved possible to prepare $Mo(acac)_3$, $Cr(acac)_3$ and $Fe(acac)_3$ from the corresponding monomeric metal carbonyl (4,5), it appeared that reaction of acetylacetonone with $Re_2(CO)_{10}$ or $Re(CO)_5Cl$ might give the desired compound. Such was not the case. Under the conditions tried, $Re_2(CO)_{10}$ did not react with acetylacetonone; and the reaction of $Re(CO)_5Cl$ with acetylacetonone gave two products, neither of which was $Re(acac)_3$.

In the meantime, Courier (1,2 4) had prepared genuine $Re(acac)_3$ and had made very extensive studies of the physical properties of $Re(acac)_3$ and $Re(hfac)_3$. This work showed that the compound of Colton et al. (2,3) was at the very least impure. The magnetic behaviour of pure $Re(acac)_3$ is as expected ($\chi_m = \text{constant value}$). In addition, Courier's work showed that $Re(acac)_3$ is extremely easily oxidized, and Courier et al. (1) suggested that Colton et al. (2,3) were most probably dealing with an oxidation product of $Re(acac)_3$. Work on identification of the oxidation products of $Re(acac)_3$

is still continuing in this laboratory (65).

Forster (66) attempted a crystallographic study of $\text{Re}(\text{acac})_3$ and $\text{Re}(\text{hfac})_3$, and although his work was incomplete, he was able to show that $\text{Re}(\text{hfac})_3$ contains at least a C_3 axis, which means that distortion of the type observed in $\text{Mn}(\text{acac})_3$ does not occur.

Because it was not possible to make $\text{Re}(\text{acac})_3$ from the rhenium carbonyl compound, and other workers in our laboratory had essentially solved the $\text{Re}(\text{acac})_3$ problem, and because preliminary experiments on the products from the reaction of $\text{Re}(\text{CO})_5\text{Cl}$ and β -diketones showed that the products were relatively involatile and insoluble, which was not the behaviour expected for the monomer complexes which we had anticipated, we decided to look at the properties and structures of these compounds.

Our justification for this course was relatively simple. Previous workers in our laboratory had studied β -diketone complexes of rhenium in formal oxidation states $\text{Re}(\text{V})$, $\text{Re}(\text{IV})$ and $\text{Re}(\text{III})$. The extension of this work to complexes of $\text{Re}(\text{I})$ gives information about low valent metal β -diketone complexes, and together with the previous work in our laboratory (1,66,24,39), makes the studies on rhenium the most extensive made on one metal in a series of oxidation states.

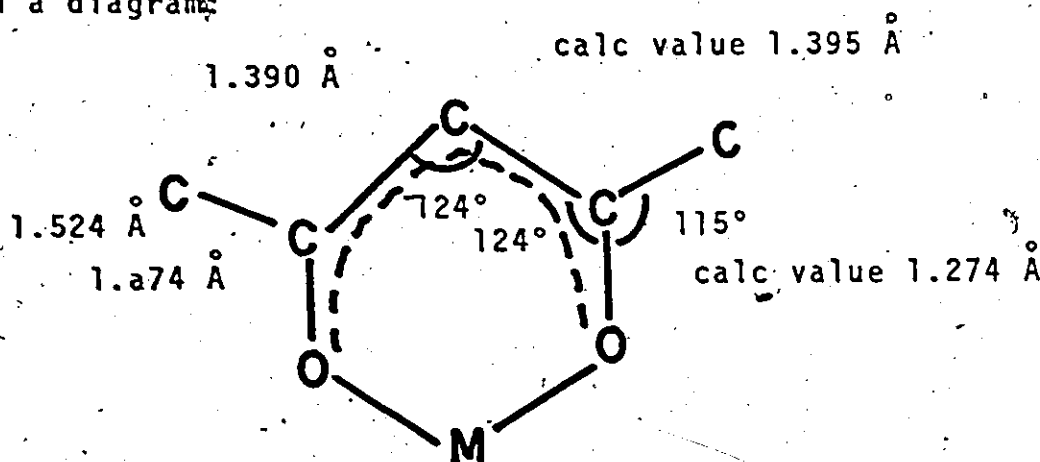
A further justification for doing the structures of our $\text{Re}(\text{I})$ compounds is that previous work by Ch'ng Wan (39).

has shown that the β -diketonates of Re III, IV and V have almost no variation in the Re-O (dik) bond lengths except for the case where the Re-O (dik) bond is opposite a multiply bonded system. If one assumes an ionic model for these compounds, one should observe a decreasing ionic radius with increasing oxidation state. Therefore, the lack of variation in bond lengths for Re-O (dik) through formal oxidation states III, IV and V is somewhat surprising. It was hoped that a study of the Re(I) system would help to clarify this problem.

CHAPTER 2

REVIEW

An extensive review of 414 papers on metal β -diketone complexes was written by Fackler (67). The main contributions of each paper are briefly mentioned, but no attempt is made to coordinate all this mass of information in order to draw some specific conclusions and predict new reaction paths and products. A much shorter but more useful collection of structural data is made by Lingafelter and Braun (68) who average the bond lengths and angles of 13 metal acetylacetonates and compare these to values calculated for a delocalized π electron system involving the OCCC O β -diketone ring but not the metal atom. These results can be summarized neatly in a diagram:



The C-O and C-C (ring) distances correspond to a bond order of nearly $1\frac{1}{2}$.

Thompson (69) has recently written a review and it is useful in that he attempts to draw some conclusions about the nature of the bonding. He said

1. ring-currents are either non-existent or do not influence molecular properties.
2. $d\pi-p\pi$ interactions do occur and do observably influence molecular properties.
3. the chelate ring is best considered as aromatic in nature with regard to chemical reactivity of the coordinated ligand."

It should be noted that he regards these conclusions as tentative and that they are based mainly on metal- β -diketonates which are bonded in the most common way (Fig. 1, I).

Gibson (70) reviews the γ -carbon bonded and γ -carbon bridging metal β -ketoenolates and discusses the strength of the M-C bond. He also reviews some of the infra-red and nmr data and concludes that γ -carbon bonded metal β -ketoenolates are most easily identified by infra-red, while compounds with a γ carbon bridge are still not reliably identified.

Forster (66) reviews the structure of $M(\text{acac})_3$ and $M(\text{hfac})_3$ compounds with particular emphasis on packing and disorder problems. Che'ng Wan (39) has reviewed the coordination numbers of metal β -ketoenolates and the type and strength of metal to β diketone bonding and has compared

the M-O (dik) bond length to that of other M-O bonds. He concludes that M-O (dik) bonds are about .04 Å shorter than M-O (single bonds); M-O (bridging dik) bonds are .1-.2 Å longer than the corresponding M-O (chelated diketone) bonds for the $(\text{Ni}(\text{acac})_2)_3$ and $(\text{Co}(\text{acac})_2)_4$ structures.

Finally, one last structural aspect may be mentioned here: the five atoms of the β -diketone, OCCCCO; usually form a plane, but this plane, in most cases, does not include the metal atom to which the β -diketone is bonded. The amount by which the metal atom is out of plane is sometimes given in Angstroms or described by the dihedral angle between the OCCCCO plane and the OMO plane. In compounds with β -diketones bonded in the manner shown in Fig. 1,I, the dihedral angle varies from 0° in $\text{Zn}(\text{dpm})_2$ (71) to 22° in $\text{Zr}(\text{acac})_4$ (72).

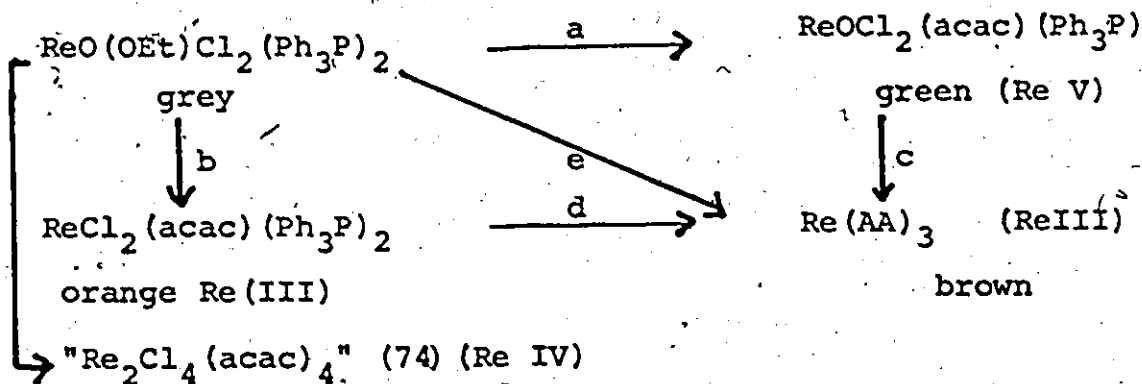
In those structures which have a μ -O bridged β -diketone, such as Fig. 1,V, the dihedral angle is usually in the 20° - 30° range. This type of bridging has always been detected only by X-ray diffraction studies.

Some of the other bonding models proposed for compounds in figure 1 have been found in only one or two compounds to date. Once a new bonding model has been established however, the trend seems to be that new compounds of this type are rapidly discovered. Infra-red and/or nmr data were used to deduce the structures of compounds II, III; VII,

X to XII. These bonding models must remain tentative, however, until they are substantiated by structural data. They may prove to be incorrect, as has been shown for example VI (fig. 1), or are still open to interpretation as in the case of examples X and XI, which I discuss in more detail in page 59.

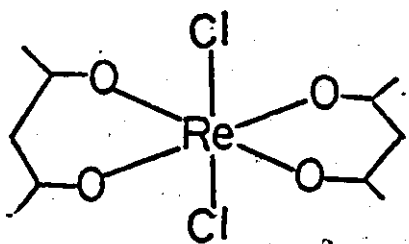
Rhenium β -ketoenolate compounds

The first β -ketoenolate complex of rhenium to be reported was trisacetylacetonatorhenium (III), $\text{Re}(\text{acac})_3$ (2,3). This has since been shown, by Courrier et al (1), to be in error, and it is probable that the original compound reported was at least partially oxidized. This is discussed at length in the introduction and we may turn our attention to a second reported method of producing $\text{Re}(\text{acac})_3$ by Lock (73). The reaction producing $\text{Re}(\text{acac})_3$ from $\text{ReO}(\text{OEt})\text{Cl}_2(\text{Ph}_3\text{P})_2$ was very complex and can best be summarized by the following scheme.



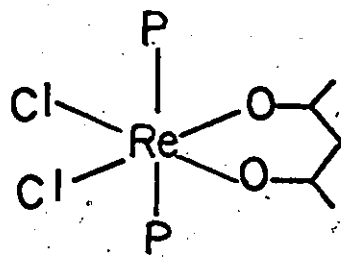
Reactions a, b and c were described as rapid, d was considered to be slower (proceeding through intermediates such as

$\text{ReCl}(\text{acac})_2(\text{Ph}_3\text{P})$ (74). The reaction was also said to produce " $\text{Re}_2\text{Cl}_2(\text{acac})_4$ " when neat acetylacetonone was used instead of a benzene solution (74). Other starting materials such as $\text{ReOCl}_3(\text{Ph}_3\text{P})_2$ could also be used to duplicate this reaction, but it was not clearly understood how the reaction could give products of Re III, IV and V with very little change in the reaction conditions. Courrier made an extensive series of these products in order to elucidate the reaction scheme and identify the stereochemistry of the products. He made the Cl, Br and I analogous as well as compounds with β -diketones other than acetylacetonone. Substitution products of these initial compounds were also studied. Over fifty compounds are mentioned by Courrier, and these include, for the first time, some nitrido-rhenium complexes with oxygen containing ligands such as $\text{ReNCl}(\text{hfac})(\text{Ph}_3\text{P})_2$ and the first pyridine β -ketoenolate complex of rhenium $\text{ReCl}_2(\text{acac})(\text{py})(\text{Ph}_3\text{P})$. While Courrier studied the chemistry of the system, some of the critical stereochemical facts required to elucidate the reaction scheme were found by Che'ng Wan who determined these three structures:



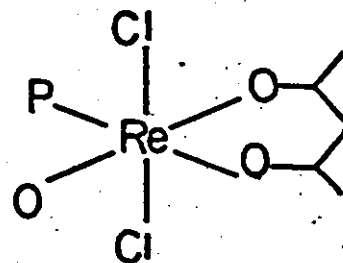
trans $\text{ReCl}_2(\text{acac})_2$

I



$\text{ReCl}_2(\text{acac})(\text{Ph}_3\text{P})_2$

II



$\text{ReOCl}_2(\text{acac})(\text{Ph}_3\text{P})$

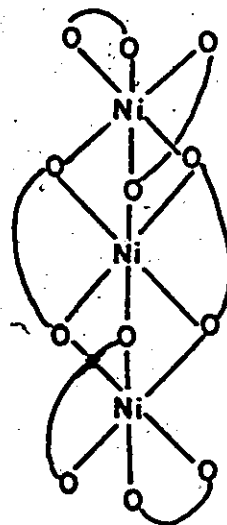
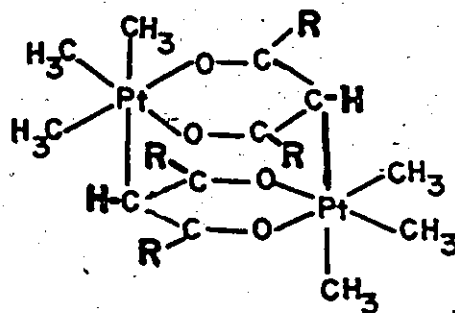
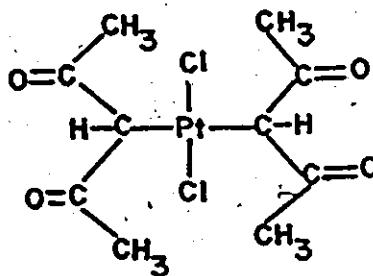
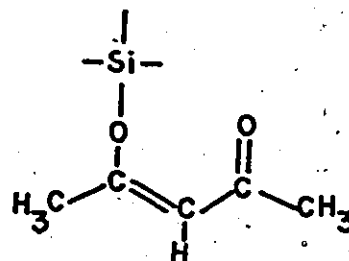
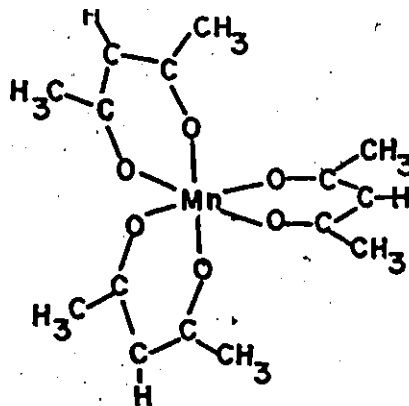
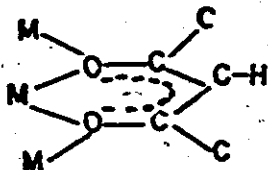
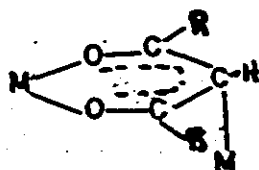
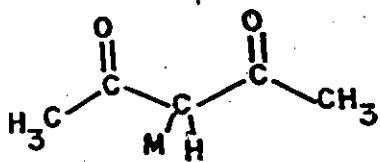
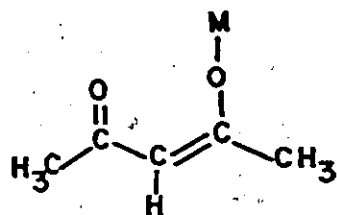
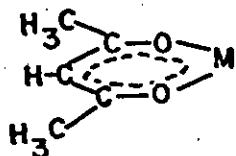
III

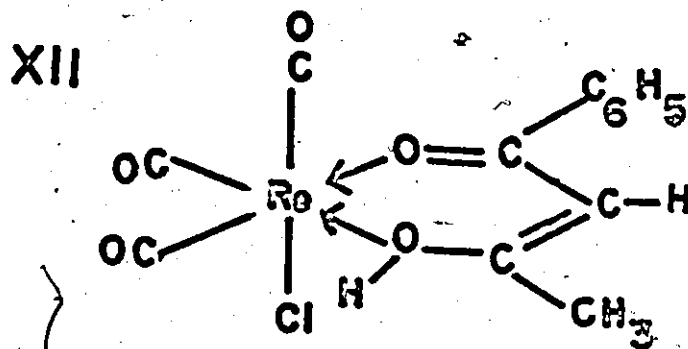
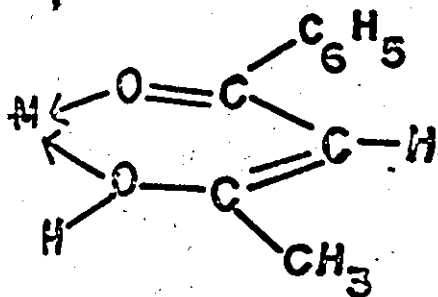
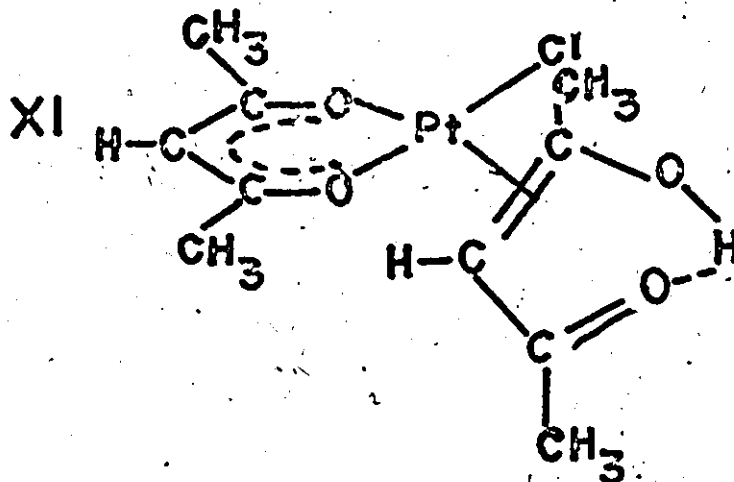
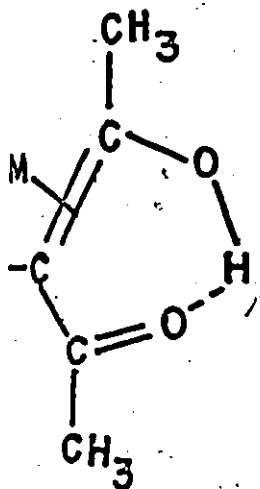
Figure 1

Metal β -diketone bonding types.

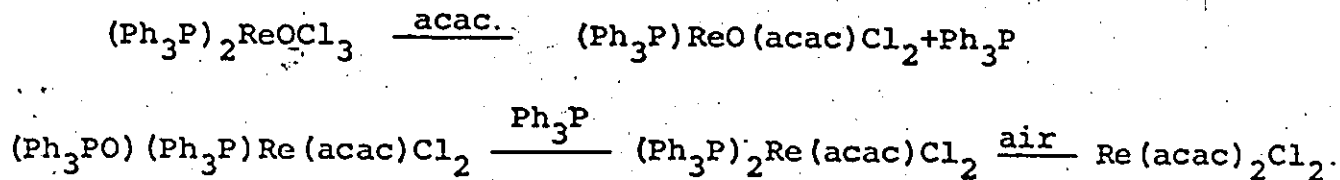
Type	Reference
I	7
II	13
III	14
IV	15
V	16
VI	17
VII	18
VIII	19
IX	19
X	20
XI	21
XII	22

ANION





The combination of structural work by Wan and chemical studies by Courrier solved the problem of the reaction scheme



My main interest in these compounds, however, arises from the lack of variation in the Re-O (dik) bond lengths, as stated in the introduction. A short table may be used to summarize some of the features of interest.

Compound	Re-O (dik) bond length in Å	Re-Cl bond length in Å	Ring C-O bond length	Ring C-C bond length	Dihe- dral angle
$\text{ReCl}_2(\text{acac})_2$	1.99(1)	2.326(8)	1.27(2)	1.39(2)	3.1°
$\text{ReCl}_2(\text{acac})(\text{Ph}_3\text{P})_2$	2.00(1), 2.04(1)	2.369(4)	1.29(2)	1.35(2)	5.7°
$\text{ReOCl}_2(\text{acac})(\text{Ph}_3\text{P})_2$	2.00(1), 2.09(1)	2.373(4)	1.24(3)	1.35(2)	17.0°

Apart from the equal (within errors) Re-O bond lengths, one may note that ring C-O and ring C-C bond lengths are close to those values given by Lingafelter for a delocalized π system in the β -diketone.

CHAPTER III

Chemistry Experiments

Physical methods

Analyses for carbon, hydrogen, nitrogen, fluorine, chlorine and sulphur were done by Galbraith Laboratories Inc., Knoxville, Tennessee, and A.B. Gygli, Toronto, Ontario. Rough rhenium and chlorine percentages and accurate rhenium-chlorine atom ratios were determined by neutron activation analysis (26). Infrared spectra were recorded for solid samples ground into a mull with Nujol. The Nujol had been dried by refluxing with phosphorus pentoxide followed by vacuum distillation. The mull samples were mounted between potassium bromide or polyethylene plates, and spectra were recorded on Perkin-Elmer 337, 521 and 301 spectrometers. Magnetic susceptibility measurements were carried out on 10 cm length powdered samples packed into 3 mm (o.d.) tubes. Calibrations were made using mercury-thiocyanatocobaltate. The measurements were made by the Gouy method, and the apparatus has been described previously (27). As all samples were diamagnetic, or had very low paramagnetism, measurements were made only at 23°C and -180°C. Corrections for the diamagnetism of the ligand were taken from Selwood (28) and Foëx (29). The value for Re(I) was obtained by comparison with other metals and extrapolation of data for other rhenium oxidation states and was assumed to be -56×10^{-6} cgsu. Mass spectra were recorded on a Consolidated Electroynamics Corp. Model 21-1108 instrument. Nuclear magnetic resonance spectra were recorded for solution samples on a Varian Associates HA 100 spectrometer. All solvents and reagents used were Reagent grade and were not purified further.

Preparation of rhenium compounds used as starting materials.

Chloropentacarbonylrhenium(I). Rhenium metal powder was converted to perrhenic acid using 30% hydrogen peroxide in a Florence flask. The resulting solution was boiled to remove any excess H_2O_2 and was neutralized with a solution of potassium hydroxide; a white precipitate of potassium perrhenate was formed. The $KReO_4$ was washed into a large beaker and converted to K_2ReCl_6 (30). The K_2ReCl_6 was then converted to $Re(CO)_5Cl$ by the method of Hieber, Schuh and Fuchs (31). The $Re(CO)_5Cl$ was recrystallized from benzene or sublimed. Note: Yields are not reported as they varied from one preparation to the next. Some unreacted $Re(CO)_5Cl$ was usually recovered from each preparation in which it was used as a starting material. Yields based on amount of $Re(CO)_5Cl$ reacted were usually at least 50%. Derivatives made by further reaction of new compounds reported here usually had a yield of near 80%.

Bis(μ -O-pentane-2,4-dionato)tricarbonylrhenium(I). (A) Chloropentacarbonylrhenium(I) (1mmole) and acetylacetone (3mmole) were refluxed in benzene (~75 ml) for 2 weeks. The pale yellow solution gradually turned dark brown. Evaporation of the solvent (~20°, ~15mm), followed by addition of ether (~100 mls) and filtration, served to remove any unreacted chloropentacarbonylrhenium(I). The filtrate was evaporated and the residues were dissolved in the minimum amount of chloroform or ether. Addition of enough petroleum ether to cause cloudiness produced a brown powder which was collected on a filter and recrystallized from methylene chloride or ether, giving small white needles.

Bis(μ -O-1,3-diphenylpropane-1,3-dionato)tricarbonylrhenium(I). (B) Chloropentacarbonylrhenium(I) (1mmole) and dibenzoylmethane (3mmole) were refluxed for 3-4 weeks in benzene (~75 mls). Bright orange crystals of the product were removed on a filter and washed with hot benzene. More product was sometimes obtained by heating the dried residues in vacuo with a heat

lamp for 2-3 hours and then washing the melt with hot benzene.

Bis(μ -O-4,4,4-trifluoro-1-phenyl-1,3-butanedionatotricarbonylrhenium(I)). (C)

Chloropentacarbonylrhenium(I) and trifluorobenzoylacetone were refluxed in benzene for 1 week. The solution was cooled, filtered and evaporated to dryness. The residues were dissolved in ether, and the solution was filtered and evaporated to dryness. These procedures served to remove any unreacted $\text{Re}(\text{CO})_5\text{Cl}$. The brown residues from the ether solution were stirred with a minimum amount of chloroform or methylene chloride for a few seconds. A brown solution was formed as the residues dissolved, leaving the yellow product as a powder in the bottom of the flask. The solid yellow product was collected on a filter as rapidly as possible because it would also dissolve within a few minutes. The brown filtrate usually contained a fair amount of the yellow product which had dissolved in the chloroform. Thus, the filtrate could be evaporated to dryness to give a brown residue from which more yellow solid could be obtained, by repeating the process of stirring with a minimum amount of solvent and filtering.

Bis(μ -O-1,1,1-trifluoro-3-thenoylacetoneatotricarbonylrhenium(I)). (D) This yellow compound was prepared by the same method as (C) using chloropentacarbonylrhenium(I) and thenoyltrifluoroacetone as starting materials.

Bis(μ -O-1,1,1-trifluoropentane-2,4-dionatotricarbonylrhenium(I)). (E) This yellow compound was prepared by the same method as (A) using chloropentacarbonylrhenium(I) and trifluoroacetylacetone as starting materials.

Bis(μ -O-1,1,1,5,5,5-hexafluoro-2,4-pentanedionatotricarbonylrhenium(I)). This yellow-orange compound was prepared by the same method as (A) using chloropentacarbonylrhenium(I) and hexafluoroacetylacetone as starting materials.

Bis(μ -chlorotricarbonyl(1-phenyl-1-hydroxobut-1-ene-3-one)rhenium(I)).

Chloropentacarbonylrhenium(I) (2g) and benzoylacetone (1.5g) were refluxed in benzene (~150 ml) for 1 day. The pale yellow solution gradually turned green. The solution was evaporated to near dryness, dichloromethane (20 ml) was added and the solution was filtered, and the filtrate evaporated to near dryness. A mixture (1:1 v/v) of dichloromethane and petroleum ether (40°-60°) was added and the resulting solution allowed to evaporate slowly over a few days to give the desired product, a yellow-green powder. The material was recrystallized from dichloromethane-petroleum ether to give crystals which were usually six-sided plates or occasionally rhomb shaped needles.

Bis(μ -chlorotricarbonyl[2-hydroxopent-2-ene-4-one]rhenium(I)).

Chloropentacarbonylrhenium(I) and acetylacetone were refluxed in benzene for 5 hours and the white product was filtered off. We have been unable to repeat this preparation.

Pentane-2,4-dionatotetracarbonylrhenium(I). (F) Compound (A) was sealed in a bomb with 200 atm. of carbon monoxide and was heated to 150°C for 24 hours. The bomb was cooled, dismantled and washed out with ether. Evaporation of the ether left the white product behind.

1,3-diphenylpropane-1,3-dionatotetracarbonylrhenium(I). The green-yellow compound was prepared similarly to (F) using compound (B) as starting material.

4,4,4-trifluoro-1-phenyl-1,3-butanedionatotetracarbonylrhenium(I). The green-yellow compound was prepared similarly to (F) using compound (C) as starting material.

1,1,1-trifluoro-3-thenoylacetone-tetracarbonylrhenium(I). The green-yellow

compound was prepared similarly to (F) using compound (D) as starting material.

1,1,1-trifluoropentane-2,4-dionatotetracarbonylrhenium(I). This pale yellow compound was prepared similarly to (F) using compound (E) as starting material.

1,3-diphenylpropane-1,3-dionatotricarbonylpyridinerhenium(I). Compound (B) and an excess of pyridine were refluxed in benzene. The orange solution turned yellow-green overnight. The solution was then evaporated to dryness. The residues were dissolved in methanol and petroleum ether (30-60°) producing an orange solution. Partial evaporation and cooling of this solution produced orange crystals which were recrystallized from ether and petroleum ether (30-60°).

1,3-diphenylpropane-1,3-dionatotricarbonyltriphenylphosphinerhenium(I). Stoichiometric quantities of compound (B) and triphenylphosphine were refluxed in benzene for 1½ hours. The hot solution was filtered and then evaporated to dryness. The residues were washed with methanol and the impure solid orange product was captured on a filter and washed with ether. These crystals were dissolved in acetone and the solution was filtered. The filtrate was allowed to evaporate slowly over 2-3 days, and orange crystals of the pure product were obtained.

1,1,1-trifluoropentane-2,4-dionatodicarbonylbis(triphenylphosphine)rhenium(I). Compound (E) and an excess of triphenylphosphine were refluxed in benzene. The green solution turned yellow-green overnight. The solution was then evaporated to dryness. The residues were dissolved in methanol and petroleum ether (30-60°). Partial evaporation and cooling of this solution produced orange crystals of the product. The product was recrystallized from ether.

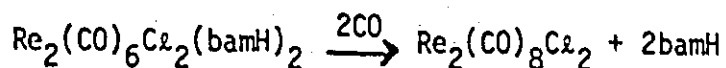
1,3-diphenylpropane-1,3-dionatodicarbonylbis(triphenylphosphine)rhenium(I).

Compound (B) and an excess of triphenylphosphine were refluxed in benzene for 12 hours. The orange solution turned orange-red within the first 2 hours. The solution was evaporated to dryness and the residues were washed with methanol, which left orange crystals of the product in the bottom of the flask. These crystals were collected on a filter and washed with ether.

1,1,1,5,5,5-hexafluoro-2,4-pentanedionatotetracarbonylrhenium(I). The yellow crystals of the product were prepared by the same method as (A) using hexafluoroacetylacetone and refluxing for only 12 hours.

Other reactions:

1) $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{bamH})_2$ was sealed in a bomb with 200 atmospheres of carbon monoxide and was heated to 150°C for 24 hours. The products were identified by infra-red spectroscopy and were $(\text{Re}(\text{CO})_4\text{Cl})_2$ and bamH.



2) $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{bamH})_2$ was refluxed in benzene with sodium carbonate for 3 days in an attempt to remove HCl and form $\text{Re}_2(\text{CO})_6\text{bam}_2$. The infra-red spectrum of the dried residues showed that no change had taken place.

3) $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{bamH})_2$ was heated in vacuo up to 135°C in a sublimation apparatus fitted with a water cooled cold finger. Initially, some bamH condensed on the cold finger. Later, some light yellow unidentified species condensed on the cold finger, it showed some carbonyl and other bands in the I.R. A brown glass, left in the bottom, can be purified to give mainly the original $\text{Re}_2(\text{CO})_6(\text{bamH})_2$.

4) $\text{Re}_2(\text{CO})_6\text{dbm}_2$ was sealed in a bomb with 200 atm. of nitrogen and was heated to 150°C for ~~24~~ hours. $\text{Re}_2(\text{CO})_6\text{dbm}_2$ was recovered unchanged.

- 5) $\text{Re}(\text{CO})_4\text{dbm}$ was sealed in a bomb with 200 atm. of nitrogen and was heated to 150°C for 24 hours. $\text{Re}_2(\text{CO})_6\text{dbm}_2$ was the only product found.
- 6) $\text{Re}(\text{CO})_2\text{dbm}(\text{Ph}_3\text{P})_2$ was heated to 185°C in vacuo in a sublimation apparatus fitted with a water cooled cold finger. The residue in the bottom is mainly $\text{Re}(\text{CO})_2\text{dbm}(\text{Ph}_3\text{P})_2$ and there are traces everywhere in the apparatus of other decomposition products, but it was not possible to obtain enough sample to identify them.
- 7) $[\text{Ph}_2\text{SRe}(\text{CO})_3\text{C}_2]_2$ and $[(\text{Ph-S-CH}_2\text{-Ph})\text{Re}(\text{CO})_3\text{C}_2]_2$ were prepared by Hieber's (22 and references therein) method. $[\text{Ph}_2\text{SRe}(\text{CO})_3\text{C}_2]_2$ was heated to 185°C in vacuo in a sublimation apparatus but no $[\text{Re}(\text{CO})_3\text{C}_2]_x$ (22) product could be found. The starting product was found unchanged in all parts of the apparatus. $[(\text{Ph-S-CH}_2\text{-Ph})\text{Re}(\text{CO})_3\text{C}_2]_2$ was heated to 230°C in vacuo in a sublimation apparatus. Again, no $[\text{Re}(\text{CO})_3\text{C}_2]_x$ could be found and the starting material was recovered everywhere in the sublimation apparatus. $[\text{Ph}_2\text{SRe}(\text{CO})_3\text{C}_2]_2$ was melted at 140°C in vacuo overnight together with some bamH . Only the starting products could be recovered. All the above in 7 were an attempt to produce Hieber's (22) compound $\text{Re}(\text{CO})_3\text{C}_2\text{bamH}$ which is described as dark red.
- 8) $\text{Re}_2(\text{CO})_6\text{acac}_2$ was refluxed in benzene with Ph_3P for two days. The solution was evaporated and methanol was added, leaving a cream coloured powder which has an infra-red spectrum identical to that of $\text{Re}(\text{CO})_2\text{acac}(\text{Ph}_3\text{P})_2$ reported by Freni et al. (25).
- 9) Details relevant to the preparation of compounds described here:
 $\text{Re}_2(\text{CO})_6(\text{dik})_2$ all use 1 mmole $\text{Re}(\text{CO})_5\text{C}_2$ and 3 mmole of the β -diketone in 75 ml. of benzene. All $\text{Re}_2(\text{CO})_6\text{C}_2(\text{dikH})_2$ use 2g $\text{Re}(\text{CO})_5\text{C}_2$ and 1.5g of the β -diketone in 150 ml. of benzene. $\text{Re}(\text{CO})_4\text{dik}$ use 100 mg of the

corresponding $\text{Re}_2(\text{CO})_6(\text{dik})_2$. $\text{Re}(\text{CO})_3(\text{dik})\text{L}$ ($\text{L} = \text{py}, \text{Ph}_3\text{P}$) and $\text{Re}(\text{CO})_2(\text{dik})(\text{Ph}_3\text{P})_2$ use 200 mg of $\text{Re}_2(\text{CO})_6(\text{dik})_2$ or $\text{Re}(\text{CO})_5\text{dik}$ in 100 ml. of benzene. Quantities may be increased proportionately to the amount of product desired.

Table 1 Analysis of Compounds

Analysis (%)

Compound	C		H		Other		M. weight		M.P. [†] C.
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
Re ₂ (CO) ₆ (acac) ₂	26.0	25.8	1.9	2.1			738	738	260
Re ₂ (CO) ₆ (dbm) ₂	43.8	44.0	2.2	2.2			988	≥820	~420
Re ₂ (CO) ₆ (tfba) ₂	32.2	33.6	1.3	1.6	11.7F	10.7F			124
Re ₂ (CO) ₆ (ttfa)	26.9	27.7	0.8	1.5	6.2S	6.5S			173
Re ₂ (CO) ₆ (tfac) ₂	22.8	22.6	1.0	1.4	13.4F	12.2F	846	846	180
Re ₂ (CO) ₆ (hfac) ₂	20.1	19.2	0.2	0.5	23.9F	22.6F	954	954	185
Re ₂ (CO) ₆ Cr ₂ bam ₂	33.4	33.2	1.9	2.2	7.6C ₂	7.6C ₂			161
Re ₂ (CO) ₆ Cr ₂ (acacH) ₂	23.7	22.7	1.7	1.8	8.8C ₂	9.8C ₂			-
Re(CO) ₄ acac	27.2	27.1	1.5	1.6					**
Re(CO) ₄ dbm	43.7	43.7	2.1	2.1					**
Re(CO) ₄ tfba	32.7	31.5	1.2	1.3	11.1F	10.2F			**
Re(CO) ₄ ttfa	27.2	28.3	1.0	0.2	11.0F 6.2S	12.0F 6.2S			**
Re(CO) ₄ tfac	24.9	24.0	0.9	0.9	12.6F	11.4F			**
Re(CO) ₄ hfac	21.4	21.3	0.2	0.2	22.6F	22.7F			103

Cont'd...

Table 1 continued

Compound	C		H		Other		M. weight		M.P. [†] C.
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
Re(CO) ₃ (dbm)(py)	48.3	48.3	2.8	2.9	2.4N	2.5N	572	572	189
Re(CO) ₃ (dbm)Ph ₃ P	57.3	57.1	3.4	3.5	4.1P	4.2P			186
Re(CO) ₂ tfac(Ph ₃ P) ₂	56.1	56.1	3.7	3.5	6.7P 6.2F	6.6P 6.1F	919	≥656	206
Re(CO) ₂ dbm(Ph ₃ P) ₂	64.3	64.3	4.1	4.6	6.3P	6.3P	989	≥726	272

* Molecular weights were determined by mass spectroscopy using a Consolidated Electroynamics Corp., Model 21-110B mass spectrometer.

† Actually decomposition temperatures except for compounds with dbm and Re(CO)₄hfac.

** These compounds do not melt but return to the corresponding dimer upon heating.

Table 2 Infrared Vibrational Spectral Data for $\text{Re}_2(\text{CO})_6\text{dik}_2$ Compounds

$\text{Re}_2(\text{CO})_6(\text{acac})_2$	$\text{Re}_2(\text{CO})_6\text{dbm}_2$	$\text{Re}_2(\text{CO})_6\text{tfba}_2$	$\text{Re}_2(\text{CO})_6\text{ttfa}_2$	$\text{Re}_2(\text{CO})_6\text{tfac}_2$	$\text{Re}_2(\text{CO})_6\text{hfac}_2$
2025 vs	2025 vs	2035 m	2035 s	2030 vs	2030 vs
1920 vs	1920 vs	1915 vs	1915 vs	1940 vs	1955 vs
1885 vs	1885 vs	1885 vs	1890 vs	1885 vs	1935 vs
1580 mW	1585 m	1600 vs	1585 s	1610 s	1600 w
1560 m	1565 s	1570 vs	1530 w	1590 sh (m)	1530 w
1520 s	1500 s	1320 sh	1510 w	1520 m	1140 broad
1281 mW	1440 m	1275 s	1400 m	1390 w	740 m
1203 vW	1307 mW	1202 s	1340 m	1309 m	720 m
1170 vW	1288 m	1158 s	1310 mW	1291 s	672 m
1153 vW	1227 mW	1118 m	1268 w	1238 m	649 m
1032 mW	1188 mW	1098 mW	1240 w	1206 s	628 w
1012 sh	1158 vW	1071 m	1200 m	1144 s	507 m
940 mW	1110 w	1028 w	1154 m	1137 s	
923 sh	1097 w	1002 w	1134 m	1086 mW	
908 sh	1069 w	908 m	1070 w	1031 m	
802 mW	1051 mW	809 m	1030 w	942 w	
792 mW	1030 w	772 vs	935 w	912 mW	
722 w	1022 m	745 w	912 w	870 m	
670 w	1002 w	718 m	872 w	808 m	
605 mW	983 w	692 s	804 w	752 w	
530 m	935 w	626 m	778 w	738 m	
518 sh	922 w	578 m	734 w	722 sh	
502 m	832 mW		726 w	662 w	
436 vW	806 vW		690 w	618 w	
412 m	782 vW		668 w	590 w	
	727 s		520 w	528 m	
	699 w			510 m	
	686 m			493 m	
	664 w			420 m	
	640 w				
	624 mW				
	548 mW				
	524 w				
	518 w				
	508 mW				
	492 mW				
	470 w				
	440 w				

Table 3 Infrared Vibrational Spectral Data for Re(CO)₄dik Compounds

Re(CO) ₄ (acac)	Re(CO) ₄ (dbm)	Re(CO) ₄ (tfba)	Re(CO) ₄ (ttfa)	Re(CO) ₄ (tfac)	Re(CO) ₄ (hfac)
2105 w	2110 w	2110 w	2110 w	2110 w	2120 m
2005 s	2005 s	2010 s	2010 s	2015 s	2048 s
1990 m	1990 m	1990 m	1990 m	1995 m	2010 s
1945 s	1945 s	1920 s	1920 s	1955 s	1940 s
1590 mw	1590 mw	1600 m	1600 m	1605 m	1630 m
1520 mw	1560 mw	1575 s	1575 s	1530 w	1605 m
1360 sh	1525 w	1530 w	1530 w	1360 sh	1555 w
1278 w	1322 w	1400 w	1400 w	1350 w	1525 w
1200 w	1300 w	1340 w	1340 w	1301 s	1350 m
1125 w	1205 w	1310 m	1310 m	1290 sh	1270 s
920 w	1158 w	1238 m	1238 m	1228 w	1253 s
780 w	775 w	1197 m	1197 m	1200 m	1237 s
748 w	724 m	1152 msh	1152 msh	1155 m	1205 sh
725 w	589 w	1145 m	1145 m	1144 m	1150 s
640 w		962 w broad	962 w broad	1022 w	1109 m
590 w		797 w	797 w	970 w	972 w
588 w		774 w	774 w	918 w	822 w
520 w		724 m	724 m	870 w	811 s
		660 w	660 w	792 w	750 w
		606 w	606 w	745 w	724 mw
		585 w	585 w	732 m	683 ms
		567 w	567 w	720 m	645 m
				668 w	607 m
				664 w	575 ms
				639 w	530 w
				518 w	500 w
				590 w	482 mw
				575 m	
				570 m	
				518 w	

Table 4 Infrared Vibrational Spectral Data for Re(CO)₆LL' Compounds

Re ₂ (CO) ₆ Cl ₂ (bamH) ₂	Re(CO) ₃ (dbm)(py)	Re(CO) ₃ (dbm)(Ph ₃ P)	Re(CO) ₂ (dbm)(Ph ₃ P) ₂	Re(CO) ₂ (tfac)(Ph ₃ P) ₂
2030 s	2010 s	2015 s	1915 s	1920 s
2025 s	1920 s	1915 s	1830 s	1940 s
1940 m	1890 s	1890 s	1590 mW	1610 m
1910 s	1580 w	1580 w	1540 m	1505 w
1895 s	1505 m	1515 ms	1515 m	1292 s
1590 m	1300 w	1300 mW	1310 w	1190 m
1560 w	1222 w	1228 w	1225 w	1142 sh
1510 m	1068 w	1155 vW	1182 w	1135 m
1305 mW	760 mW	1095 w	1158 w	750 sh
1230 mW	718 w	1025 w	1094 w	738 m
1221 sh	697 w	988 vW	1088 w	720 sh
1190 w	685 w	940 vW	1025 w	692 ms
1162 w	635 w	890 vW	988 w	583 w
1105 w	520 w	754 mW	753 w	538 sh
1130 w	490 w	740 w	742 m	525 mW
1008 wsh		720 m	736 m	515 ms
1000 w		692 mW	718 v	498 mW
840 w		682 w	700 sh	
830 w		648 w	688 m	
773 ms		638 w	633 w	
738 w		627 w	623 w	
722 w		608 w	613 w	
698 m		545 vW	587 w	
658 mW		523 m	512 ms	
638 w			497 m	
582 w				
515 w				
500 w				
266 v	Re-Cl			

Table 5

Mass Spectrum of $\text{Re}_2(\text{CO})_6(\text{tfac})_2$ Mass Spectrum of $\text{Re}_2(\text{CO})_6(\text{acac})_2$

Mass	% Abundance [†]	Ion	Mass	% Abundance*	Ion
738	3.2	$\text{Re}_2(\text{CO})_6(\text{acac})_2^+$	846	16	$\text{Re}_2(\text{CO})_6(\text{tfac})_2^+$
682	2.5	$\text{Re}_2(\text{CO})_4(\text{acac})_2^+$	827	0.2	above minus 1 F
654	2.3	$\text{Re}_2(\text{CO})_3(\text{acac})_2^+$	799	1	$\text{Re}_2(\text{CO})_5(\text{tfac})_2^+$ minus 1 F
626	0.2	$\text{Re}_2(\text{CO})_2(\text{acac})_2^+$	790	8	$\text{Re}_2(\text{CO})_4(\text{tfac})_2^+$
598	0.5	$\text{Re}_2(\text{CO})(\text{acac})_2^+$	762	7	$\text{Re}_2(\text{CO})_3(\text{tfac})_2^+$
570	1.4	$\text{Re}_2(\text{acac})_2^+$	734	0.2	$\text{Re}_2(\text{CO})_2(\text{tfac})_2^+$
385	0.3	$\text{Re}(\text{acac})_2^+$	706	0.4	$\text{Re}_2(\text{CO})(\text{tfac})_2^+$
370	69.7	$\text{Re}(\text{CO})_3(\text{acac})^+$	678	0.4	$\text{Re}_2(\text{tfac})_2^+$
342	34.6	$\text{Re}(\text{CO})_2(\text{acac})^+$	424	100	$\text{Re}(\text{CO})_3(\text{tfac})^+$
314	5.5	$\text{Re}(\text{CO})(\text{acac})^+$	396	54	$\text{Re}(\text{CO})_2(\text{tfac})^+$
299	0.7	$\text{Re}(\text{CO})\text{OC}(\text{CH}_3)\text{CHCO}^+$	368	2	$\text{Re}(\text{CO})(\text{tfac})^+$
287	14.2	$\text{Re}(\text{acac})\text{H}^+$	340	70	$\text{Re}(\text{tfac})^+$
286	100	$\text{Re}(\text{acac})^+$	320	8	$\text{Re}(\text{tfac})^+$ minus 1 HF
271	3.5	$\text{ReOC}(\text{CH}_3)\text{CHCO}^+$	292	8	$\text{Re}(\text{tfac})^+$ minus 2 HF
268	1.6	$\text{ReOC}(\text{C})\text{CHCO}^+$	241	19	ReOF_2^+
258	22.1	$\text{ReO}_2\text{C}_2\text{CH}_3^+$	236	8	ReO_2F^+

Cont'd..

Mass Spectrum of $\text{Re}_2(\text{CO})_6(\text{acac})_2$

Mass	% Abundance	Ion
256	35.8	above + $\text{ReO}_2\text{C}_2\text{CH}^+$
254	21.2	$\text{ReO}_2\text{C}_2\text{CH}^+$
243	10.3	$\text{ReO}_2\text{C}_2 + \text{ReOC}(\text{CH}_3)\text{CH}^+$
241	21.2	ReO_2C_2^+
231	5.4	ReO_2C^+
230	6.4	ReOCCH_3^+
203	7.0	ReO^+
187	7.6	Re^+
100	6.4	$(\text{acac})\text{H}^+$
85	7.6	$\text{OCCH}_2\text{COCH}_3^+$
43	23.9	CH_3CO^+
39	4.6	HCCO^+
28	6.7	CO^+

[†]Relative to peak at mass 286

Mass Spectrum of $\text{Re}_2(\text{CO})_6(\text{tfac})_2$

Mass	% Abundance	Ion
203	9	ReO^+
187	6	Re^+
69	12	CF_3^+
50	2	CF_2^+
43	100	CH_3CO^+
28	38	CO^+
20	3	HF^+

* Relative to peak at mass 43

Mass Spectrum of $\text{Re}_2(\text{CO})_6(\text{dcm})_2$

Mass	% Abundance**	Ion
818	0.3	$\text{Re}_2(\text{dcm})_2^+$
494	90.3	$\text{Re}(\text{CO})_3(\text{dcm})^+$
466	5	$\text{Re}(\text{CO})_2(\text{dcm})^+$
438	29	$\text{Re}(\text{CO})(\text{dcm})^+$
410	34	$\text{Re}(\text{dcm})^+$
382	45	$\text{ReOC}_2\text{H}(\text{Ph})_2^+$
380	84	above + $\text{ReO}_2\text{C}_2\text{PhC}_6\text{H}_4^+$
378	52	$\text{ReO}_2\text{C}_2\text{PhC}_6\text{H}_4^+$
224	37	dcmH^+
223	36	dcm^+
208	7	$\text{PhCCH}_2\text{C}(\text{Ph})\text{O}^+$
207	7	$\text{PhCCHC}(\text{Ph})\text{O}^+$
192	14	$\text{PhCCH}_2\text{CPh}^+$
191	6	PhCCHCPh^+
77	100	Ph^+

** Relative to peak at mass 77

Mass Spectrum of $\text{Re}(\text{CO})_2(\text{dcm})(\text{Ph}_3\text{P})_2$

Mass	% Abundance***	Ion
755	8	$\text{Re}(\text{CO})_3(\text{dcm})(\text{Ph}_3\text{P})^+$
728	31	$\text{Re}(\text{CO})_2(\text{dcm})(\text{Ph}_3\text{P})^+$
672	100	$\text{Re}(\text{dcm})(\text{Ph}_3\text{P})^+$

*** Relative to peak at mass 672

Mass Spectrum of $\text{Re}(\text{CO})_3(\text{dcm})(\text{py})$

Mass	% Abundance***	Ion
573	29	$\text{Re}(\text{CO})_3(\text{dcm})(\text{py})^+$
545	19	$\text{Re}(\text{CO})_2(\text{dcm})(\text{py})^+$
494	100	$\text{Re}(\text{CO})_3(\text{dcm})^+$
483	28	$\text{Re}(\text{dcm})(\text{py})^+$
466	78	$\text{Re}(\text{CO})_2(\text{dcm})^+$
438	34	$\text{Re}(\text{CO})(\text{dcm})^+$
410	33	$\text{Re}(\text{dcm})^+$

*** Relative to peak at mass 494

Mass Spectrum of $\text{Re}(\text{CO})_2(\text{tfac})(\text{Ph}_3\text{P})_2$

Mass	Abundance ^{††}	Ion
686	1	$\text{Re}(\text{CO})_3(\text{tfac})(\text{Ph}_3\text{P})^+$
658	37	$\text{Re}(\text{CO})_2(\text{tfac})(\text{Ph}_3\text{P})^+$
630	4	$\text{Re}(\text{CO})(\text{tfac})(\text{Ph}_3\text{P})^+$
602	100	$\text{Re}(\text{tfac})(\text{Ph}_3\text{P})^+$

^{††}Relative to peak at mass 602

In any multiplet only the strongest peak is reported. The ratio in all multiplets agreed satisfactorily with the calculated values.

CHAPTER IV

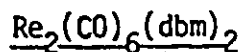
The Structure of $\text{Re}_2(\text{CO})_6(\text{dbm})_2$

Since usual physical methods (IR, nmr, mass spectra and magnetic measurements) did not reveal the structure of the $\text{Re}_2(\text{CO})_6(\text{dik})_2$ series of compounds (see Chapter VI), a single crystal X-ray determination was undertaken. $\text{Re}_2(\text{CO})_6(\text{acac})_2$ was chosen first as it had the smallest number of atoms in the molecule in this series. It proved to be disordered or twinned, however, and the structure of $\text{Re}_2(\text{CO})_6(\text{dbm})_2$ was solved instead. The results of both crystallographic studies of the $\text{Re}_2(\text{CO})_6(\text{dik})_2$ series are reported here.

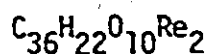
$\text{Re}_2(\text{CO})_6(\text{acac})_2$

Crystallography: $\text{Re}_2(\text{CO})_6(\text{acac})_2$. A crystal of $\text{Re}_2(\text{CO})_6(\text{acac})_2$ was mounted along the needle axis. Integrated Weissenberg photographs were taken of the (hnl) layers ($n=0-6$) with $\text{CuK}\alpha$ radiation and an integrated precession photograph was taken with $\text{MoK}\alpha$ radiation of the $(0kl)$ zone and a further precession photograph of the $(h0l)$ layer was recorded for another crystal. Systematic absences were observed for hkl ($h+l=2n+1$) and a mirror plane or two fold axis was apparent on all photographs. Assuming the crystal was orthorhombic, possible space groups were $C222(D_2^6, \text{No. 21})$, $Cmm2(C_{2v}^{11}, \text{No. 35})$, $Amm2(C_{2v}^{14}, \text{No. 38})$, $Cmmm(D_{2h}^{19}, \text{No. 65})$. Patterson maps using all of these space groups did not show any self-consistent position for the rhenium atom. Trial positions were used for the rhenium atom but the

lowest value of R_1^* obtained was 0.47. Photographs taken in the (hk0) direction showed peculiar radial streaks as though two crystals were present and out of alignment by $1^\circ 40'$. Approximately 20 crystals from different recrystallizations were examined by X-ray diffraction and all showed this effect. The apparent unit cell dimensions were $a = 15.26(1)$, $b = 16.01(1)$, $c = 17.68(1) \text{ \AA}$ (calibrated with a crystal of rutile (TiO_2)) $a = 4.5929(5) \text{ \AA}$, $c = 2.9591(3) \text{ \AA}$ (32). Detailed examination of the photographs suggested that the crystals were either twinned, or that disorder was present giving a higher pseudo-symmetry. No further X-ray studies were made of this compound.



Crystallography: $\text{Re}_2(\text{CO})_6(\text{dbm})_2$. A single crystal $0.2 \times 0.08 \times 0.12 \text{ mm}^3$, which showed complete extinction every 90° when ~~rotated~~ through a polarizing microscope was used for initial X-ray studies. A series of Weissenberg and precession photographs showed that the crystal was monoclinic, and the systematic absences $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$ showed that the space group was $P2_1/c$. Precession photographs of the (100) and (010) zones taken with $\text{MoK}\alpha$ radiation and calibrated with the diffraction pattern of a single crystal of TiO_2 (rutile) were used to determine the unit cell parameters. The density of a few crystals was measured by flotation in a bromoform-chloroform mixture.



f.w. 986.98

Monoclinic, $a = 11.988(8)$, $b = 14.441(9)$, $c = 10.298(7) \text{ \AA}$, $\beta = 115.25(7)^\circ$, $V = 1612 \text{ \AA}^3$, $\rho_0 = 2.02$, $Z = 2$, $\rho_c = 2.03$ (20°C , $\text{MoK}\alpha$, $\lambda = 0.71069 \text{ \AA}$), $P2_1/c$

$$* R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_2 = \left\{ \frac{\sum |F_o^2 - F_c^2|}{\sum (F_o)^2} \right\}^{1/2}$$

(C_{2h}⁵, No. 14).

Six layers perpendicular to [T02] were recorded on an integrating Weissenberg camera; 4 layers perpendicular to [010] and eight layers perpendicular to [100] were recorded on an integrating precession camera. All photographs except the first three layer photographs on the Weissenberg camera were taken with MoK α radiation. The latter were taken with CuK α radiation. The intensities of all reflections were measured on a Joyce-Loebl microdensitometer. All data were corrected for Lorentz and polarization effects, but no corrections were made for absorption. These data were used to solve the crystal structure although, the CuK α Weissenberg data (absorption errors) and (0k ℓ) and (h0 ℓ) data (poor picture quality) were removed in later stages of the refinement (see below). Thus the original data set of ~2800 reflections was reduced to 1436 of which 966 were observed. After the structure had been solved the data were retaken using a Syntex PT automatic diffractometer. A single crystal of Re₂(CO)₆-(dbm)₂ ground into a sphere of 0.15 mm radius was used. Data were recorded using Zirconium-filtered MoK α radiation which was made monochromatic by using the 002 reflection from highly oriented graphite. The intensities were measured by the $\theta/2\theta$ scan technique up to a value of $2\theta = 45^\circ$. Counts were 2θ below K α_1 and above K α_2 and the background was counted on both sides. Peaks less than $3\sigma^*$ above the background were called unobserved, and peaks less than the background were rejected. The intensity of a standard reflection was measured every 50 reflections. It showed a deviation of $\pm 3.8\%$. The linear absorption coefficient for the compound for MoK α radiation was 81 cm⁻¹. The data were corrected for Lorentz and polarization effects but not absorption; the absorption coefficients ranged from 5.35 to 4.95.

* σ = square root of averaged peak and background counts.

However, the error from neglect of absorption correction will be less than this since the data were collected in three batches (1, $\theta = 0-12$; 2, $\theta = 11-17$; 3, $\theta = 17-23$) and each batch was refined with its own scale constant. Thus the maximum error which can arise from neglect of the absorption correction is 3%.

Solution and Refinement of the Structure

Using Patterson maps for the (T02), (100) and (010) zones it was possible to locate the rhenium atom. Using all the film data, refinement of the rhenium atom parameters for two cycles gave $R_1 = 0.16$. The shortest Re-Re distance was 3.5 Å suggesting a dimeric unit. Subsequent electron density and electron difference syntheses, with calculations based on known geometries for β -diketone and phenyl groups, revealed all the remaining atoms, except the hydrogen atoms. Further refinement, after elimination of $\text{CuK}\alpha$ and poor film data, and using a Cruickshank weighting scheme (33) with the weights set equal to $(6I - F_0 + 0.013 F_0^2)^{-1}$ for observed reflections and zero weight for unobserved reflections*, was terminated at $R_2 = 0.101$. At this point the main features of the structure were apparent but M-C=O groups were bent ($170^\circ(2)$) and the phenyl groups were badly distorted (C-CI ranged from 1.28 Å to 1.52 Å and C-C-C angles ranged from 107° to 126°). However, difference maps showed no residual peaks at more than $\pm 1.5e/\text{Å}^3$ and no parameter shifted by more than 1/3 of its estimated standard deviation in the last few cycles of refinement. At this point the data were retaken on the diffractometer and only diffractometer data were used in subsequent refinements. The new set consisted of 1563 independent reflections, of which 1295 were observed.** One cycle of refinement of the diffractometer data using the

* see page 81 ** see page 38

parameters determined above and varying only the scale constants dropped R_2 to 0.07. Using a Cruickshank weighting scheme with weights equal to $(29 - 0.6 F_0 + 0.004 F_0^2)^{-1}$ for observed reflections and zero for unobserved reflections, and allowing all the parameters listed in Table 6 to vary dropped R_2 to 0.0427 when refinement was terminated. In all the refinement cycles of diffractometer data, which were done using the full matrix least squares programme CUDLS written for the CDC-6400 computer by J. S. Stephens, the rhenium scattering curve of Cromer (34), including anomalous dispersion corrections (35) was used. The oxygen scattering curve was also that of Cromer, and that for carbon was taken from the International Tables (36). No anomalous dispersion corrections were applied to carbon or oxygen.

In the final cycle of refinement no parameter shifted by more than 1/10 of its estimated standard deviation and a series of electron density difference maps through the unit cell showed no residual peaks outside $\pm 1 \text{ e}/\text{\AA}^3$. The final set of atom parameters is given in Table 6 and a comparison of $|F_o|$ and $|F_c|$ is given in Appendix D.

Results and Discussion

The principal interatomic distances and angles are listed in Table 7 and the molecule is illustrated in Figure 2. The molecule is dimeric (based on the rhenium atoms) and the two halves are centrosymmetrically related. Each rhenium atom is six-coordinate, being attached to atoms at the apices of a very rough octahedron. The positions are filled by three mutually cis carbonyl groups and two further positions are filled by the oxygen atoms of a chelated β -ketoenolate group. The final position is filled by one of the oxygen atoms from the β -ketoenolate

group chelated to the other rhenium atom which thus forms a bridge between the two rhenium atoms. The rhenium-rhenium distance of 3.494(1) Å is too long to allow any significant metal-metal interaction. Bridging by a β -ketoenolate group through an oxygen atom attached to two metal atoms has been observed previously in $[\text{Ni}(\text{acac})_2]_3$ (16) and $[\text{Co}(\text{acac})_2]_4$ (37), but it is only recently that dimeric compounds have been shown to have this form of bridging (39). It is of interest to compare features of the bridging section of $[\text{Pr}(\text{thd})_3]_2$ (38) and our compound. The bridges in both compounds are asymmetric. The distance of the oxygen atom to the rhenium to which it is chelated (2.162(9) Å) is significantly shorter than the distance to the other rhenium atom (2.204(7) Å). For the praseodymium compound the situation is reversed, the corresponding distances, which are much larger, being 2.59(2) Å and 2.47(2) Å. The two Re-O (chelated) distances do not differ significantly but all Re-O distances appear to be significantly longer than the Re-O (β -ketoenolate) distances in $\text{Re}(\text{acac})_2\text{Cl}_2$, $\text{Re}(\text{acac})\text{Cl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ and $\text{ReOCl}_2(\text{acac})\text{P}(\text{C}_6\text{H}_5)_3$ (23,39) where the average distance is 2.02(1) Å.

Long Pr-O distances were also observed by Erasmus et al. (38) for $[\text{Pr}(\text{thd})_3]_2$, who argued that the cause was the combination of the 70° angles needed in a seven-coordinate structure and the need to keep the O-O distances above 2.8 Å. Similar steric requirements may be the cause of the longer Re-O distance in our compound, since the $\text{O}(2)\text{-Re-O}(2)_i$ angle is 74°, and the $\text{O}(2)\text{-O}(2)_i$ distance is significantly shorter (2.62(2) Å) than that observed in $[\text{Pr}(\text{thd})_3]_2$.

Other possible reasons for the longer Re-O distance in our compound may be the destruction of any $\pi\pi\text{-d}\pi$ interaction between the β -keto-

enolate ring and the metal since, as the data in Table 8 show, the dihedral angle between the plane of the β -ketoenolate ring and the MO_2 (chelated) plane is 37° , the largest value ever observed for a β -ketoenolate complex. The comparable angle for $[\text{Pr}(\text{thd})_3]_2$ is 29° .

The steric requirements of the bridging oxygen atoms and consequently the remaining chelated oxygen atoms cause a reduction in the OReO angles from the ideal octahedral angle of 90° by from 6 - 16° ($80.0(3)$, $84.1(3)$, $73.7(3)^\circ$). However, the carbonyl groups remain nearly perpendicular to each other (C-Re-C angles $88.0(6)$, $89.9(6)$, $86.5(7)$) so that the angles at rhenium between the carbonyl groups and the oxygen atoms are opened up from 90° ($93.0(5)$ to $100.9(5)$). The maximum distortion in all cases are in the $\text{O}(2)$, $\text{O}(2)$, $\text{Re C}(17)$, $\text{C}(18)$ plane:

The $\text{Re-C}\equiv\text{O}$ systems are essentially linear ($171(4)$, $178(1)$, $178(1)^\circ$) and the Re-C bond lengths ($1.87(1)$ Å average) and $\text{C}\equiv\text{O}$ bond lengths ($1.18(2)$ Å average) are in good agreement with those found previously in $(\text{B}_9\text{C}_2\text{H}_{11})\text{Re}(\text{CO})_3$ (40), $\text{HRe}_2\text{Mn}(\text{CO})_{12}$ (41) and $(\text{C}_8\text{H}_7)\text{Re}(\text{CO})_3$ (42). The corresponding angles and bond lengths within the β -ketoenolate ring are not significantly different from the average values found for a number of β -ketoenolate structures (43), but the C_1C_3 distance does appear to be significantly longer than the C_2C_3 distance (see below). The bond lengths and angles found within the phenyl rings are normal.

The planarity of certain groups of atoms within the molecule has been tested and the results are presented in Table 8, together with the dihedral angles between the planes. Both phenyl rings are essentially planar, as expected, and are quite markedly twisted from the plane of the β -ketoenolate ring, plane 3 by 25° and plane 4 by 22° . This twist

may arise from a simple rotation about the C(2)-C(10) and C(1)-C(4) bonds (ϕ) or a tilt of the C(4)C(7) and C(13)C(10) axes out of the plane of the β -ketoenolate ring at either C(4) and C(10) or C(1) and C(2) (θ). The results in the second part of Table 8, provide information which allows separation of the two twist components.

Plane two is bent at C(1) ($\theta = 12^\circ$) and plane three is bent at C(2) ($\theta = 3^\circ$). Both plane 3 and plane 4 are rotated about the C(1)C(4) and C(2)C(10) axes ($\phi \sim 26^\circ$). An examination of the packing diagram (Fig 3) suggests that the twists are probably necessary to allow the most efficient packing. The distortion at C(1) (θ) may be the reason for the apparent non-equivalence of the C(1)C(3) and C(2)C(3) distances. The bend will tend to affect the overlap at C(1), weakening the C(1)C(3) bond, and causing a strengthening of the C(2)C(3) bond, as is observed. The errors in the CO(diketone) distances are such that it is not possible to say whether any similar effect is reflected in these bonds.

As illustrated in Figure 3, the molecules are packed almost in layers parallel to the a c plane, the centers of the layers lying approximately in the unit cell a c face and half-way along b. Within the layers packing in the c direction is determined by the β -ketoenolate system (including the phenyl rings). The molecules are arranged such that the β -ketoenolate on one side of the molecule lies directly above the opposite β -ketoenolate group on the next molecule. Thus, considering only the β -ketoenolate parts of the molecule, the molecules are stacked like tiles on a roof, and are tilted with respect to the c direction. Considering alternate layers in the b direction the molecules are tilted in opposite directions with respect to the c direction. Contact in the b direction is

provided primarily by the phenyl rings although one carbonyl group in each asymmetric half of the molecule is sandwiched between two phenyl rings, one from its own molecule and one from another.

Contact in the b direction is between both carbonyl and phenyl groups, with carbonyl groups on a molecule interleaving with carbonyl groups on molecules both above and below, and phenyl groups contacting only phenyl groups in the other molecules.

Table 6 Atomic Parameters* for $\text{Re}_2(\text{CO})_6(\text{dbm})_2$

	<u>Coordinates</u>			U_u^\ddagger +
	x	y	z	
Re	.11200(5)	.08530(3)	.07941(5)	
O(1)	.2041(8)	-.0312(5)	.2101(9)	40(2)
O(2)	-.0427(7)	.0177(5)	.0951(8)	29(2)
O(3)	-.0337(9)	.2475(7)	-.106(1)	60(2)
O(4)	.188(1)	.2110(8)	.336(1)	71(3)
O(5)	.347(1)	.1518(7)	.059(1)	61(3)
C(1)	.181(1)	-.0656(8)	.311(1)	37(3)
C(2)	-.037(1)	-.0137(8)	.220(1)	30(3)
C(3)	.067(1)	-.0473(9)	.324(1)	37(3)
C(4)	.279(1)	-.1249(9)	.415(1)	35(3)
C(5)	.396(1)	-.1160(9)	.428(2)	51(3)
C(6)	.495(2)	-.173(1)	.528(2)	67(5)
C(7)	.464(2)	-.236(1)	.609(2)	69(4)
C(8)	.347(2)	-.245(1)	.593(2)	64(4)
C(9)	.250(1)	-.190(1)	.495(2)	53(4)
C(10)	-.157(1)	-.0107(8)	.232(1)	35(3)
C(11)	-.245(1)	.0531(9)	.148(2)	47(4)
C(12)	-.351(2)	.057(1)	.153(2)	56(4)
C(13)	-.381(2)	-.004(1)	.248(2)	51(4)
C(14)	-.293(2)	-.066(1)	.330(2)	59(4)
C(15)	-.179(1)	-.0701(9)	.326(1)	36(3)
C(16)	.022(1)	.1841(9)	.963(1)	35(3)
C(17)	.157(1)	.1633(9)	.235(1)	41(3)
C(18)	.254(1)	.1273(8)	.064(1)	33(3)

* Estimated standard deviations in parentheses.

‡ Thermal parameters are in $(\text{\AA})^2 \times 10^3$

* Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	31.5	30.0	29.0(3)	0.0(3)	17.9	1.3(3)

Table 7 Bond Distances in $\text{Re}_2(\text{CO})_6(\text{dbm})_2$ *

Bonded atoms	Length (Å)	Bonded atoms	Length (Å)
Re-C(16)	1.88(1)	C(2)-C(3)	1.34(2)
Re-C(17)	1.84(1)	C(4)-C(5)	1.37(2)
Re-C(18)	1.88(2)	C(5)-C(6)	1.45(2)
Re-O(1)	2.143(8)	C(6)-C(7)	1.39(3)
Re-O(2)	2.162(9)	C(7)-C(8)	1.35(3)
Re-O(2) _i	2.204(7)	C(8)-C(9)	1.41(2)
C(16)-O(3)	1.17(2)	C(9)-C(4)	1.38(2)
C(17)-O(4)	1.18(2)	C(10)-C(11)	1.39(2)
C(18)-O(5)	1.19(2)	C(11)-C(12)	1.40(3)
O(1)-C(1)	1.29(2)	C(12)-C(13)	1.41(3)
O(2)-C(2)	1.34(2)	C(13)-C(14)	1.37(2)
C(1)-C(4)	1.49(2)	C(14)-C(15)	1.39(3)
C(2)-C(10)	1.49(2)	C(15)-C(10)	1.40(2)
C(1)-C(3)	1.45(2)		

* Subscript _i refers to the atom related by a center of symmetry to the corresponding atom listed in Table 5. Estimated standard deviations in parentheses.

Bond Angles in $\text{Re}_2(\text{CO})_6(\text{dbm})_2$

Bonded atoms	Angle (deg)	Bonded atoms	Angle (deg)
O(1)-Re-O(2)	80.0(3)	Re-C(17)-O(4)	178(1)
O(1)-Re-O(2) _i	84.1(3)	Re-C(18)-O(5)	171(4)
O(1)-Re-C(16)	176.3(5)	C(9)-C(4)-C(5)	121(1)
O(1)-Re-C(17)	93.0(5)	C(4)-C(5)-C(6)	121(2)
O(1)-Re-C(18)	93.7(5)	C(5)-C(6)-C(7)	117(2)
O(2)-Re-O(2) _i	73.7(3)	C(6)-C(7)-C(8)	122(2)
O(2)-Re-C(16)	96.4(5)	C(7)-C(8)-C(9)	122(2)
O(2)-Re-C(17)	98.8(6)	C(8)-C(9)-C(4)	118(2)
O(2)-Re-C(18)	172.0(4)	C(15)-C(10)-C(11)	121(2)
O(2) _i -Re-C(16)	94.4(4)	C(10)-C(11)-C(12)	121(2)
O(2) _i -Re-C(17)	172.3(6)	C(11)-C(12)-C(13)	118(1)
O(2) _i -Re-C(18)	100.9(5)	C(12)-C(13)-C(14)	121(2)
C(16)-Re-C(17)	88.0(6)	C(13)-C(14)-C(15)	122(2)
C(16)-Re-C(18)	89.9(6)	C(14)-C(15)-C(10)	118(1)
C(17)-Re-C(18)	86.5(7)	O(1)-C(1)-C(3)	123(1)
Re-O(2)-Re _i	106.3(4)	O(1)-C(1)-C(4)	116(1)
Re-O(2)-C(2)	122.1(6)	C(3)-C(1)-C(4)	122(1)
Re _i -O(2)-C(2)	113.7(6)	C(1)-C(4)-C(5)	119(1)
O(2)-C(2)-C(3)	122(1)	C(1)-C(4)-C(9)	120(1)
O(2)-C(2)-C(10)	114(1)	C(2)-C(10)-C(11)	118(1)
C(3)-C(2)-C(10)	123(1)	C(2)-C(10)-C(15)	120(1)
C(2)-C(3)-C(1)	126(1)	C(1)-O(1)-Re	126(1)
Re-C(16)-O(3)	178(1)		

Table 8 Selected Planes* of Atoms in $\text{Re}_2(\text{CO})_6(\text{dbm})_2$

Type	Planes	Equation
Re 0(1) 0(2)	A	$-.20668x + .53029y + .82224z = 1.05592$
0(1) 0(2) C(1) C(2) C(3)	B	$.10774x + .90206y + .41794z = .52470$
C(4) C(5) C(6) C(7) C(8) C(9)	C	$-.13992x + .68533y + .71466z = 1.30518$
C(10) C(11) C(12) C(13) C(14) C(15)	D	$.05848x + .68012y + .73077z = 1.31273$

Dihedral angles between planes

Pair of planes	Dihedral angle
A B	37°
B C	25°
B D	22°
C D	11°

Distances in Å from ring B of selected atoms
(the atoms defining ring B are not more than .08Å out of plane)

Atom	distance(Å)	Atom	distance(Å)
C(4)	-.37	C(10)	-.08
C(5)	-.06	C(11)	.36
C(7)	-.91	C(13)	-.22
C(9)	-.98	C(15)	-.55
		Re	1.00

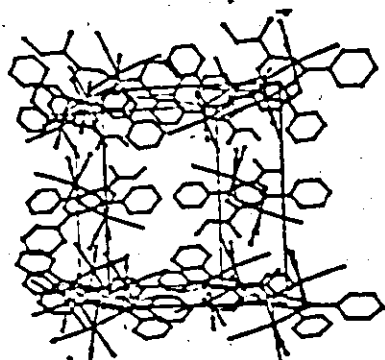
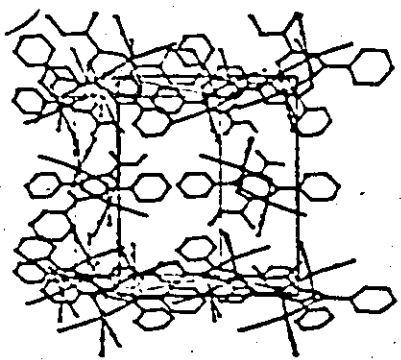
* All planes, except A which is defined uniquely, are least squares planes determined by the programme PALS written by P.G. Ashmore for the CDC 6400. The programme transforms the cell into an orthogonal cell corresponding to the crystallographic a, b, c* axes.

Figure 2

The molecular structure of $\text{Re}_2(\text{CO})_6(\text{dbm})_2$. (The labelling of atoms corresponds to that used in Table 6.)

Figure 3

Stereogram (stereoscopic pair of perspective projections) of $\text{Re}_2(\text{CO})_6(\text{dbm})_2$. The contents of one unit cell are shown with some projection outside the cell to show the packing. b and a are parallel to the side and top of the page respectively, and the view is down c*.



CHAPTER V

The Structure of $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{bamH})_2$

The second type of compound obtained from the reaction of $\text{Re}(\text{CO})_5\text{Cl}$ with β -ketoenols possessed unusual physical properties which were unexplainable by the data available (see Chapter VI). Thus it became imperative to solve the structure of a $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{dikH})_2$ compound to better understand the nature of the reactions of $\text{Re}(\text{CO})_5\text{Cl}$ with β -ketoenols.

$\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{bamH})_2$

Crystallography: A piece of acicular crystal was sandpapered by hand to a sphere of 0.2 mm diameter. The crystal was shown by precession photographs to be monoclinic, and with proper choice of the a and c axes, the systematic absences $hk\ell$, $h+k = 2n+1$, $h0\ell$, $\ell = 2n+1$ revealed the space group was $C2/c$ or Cc . The former space group was suggested by the Patterson syntheses which showed rhenium atoms related by a center of symmetry and the choice was confirmed by the successful solution of the structure. Accurate unit cell parameters were obtained by least squares refinement of the output from a Syntex P1 automatic diffractometer which centered on fifteen reflections.

$\text{Re}_2(\text{CO})_6(\text{bamH})_2$ f.w. 935.2
Monoclinic, $a = 14.77(2)$, $b = 17.98(2)$, $c = 13.48(2)$ Å, $\beta = 124.34(9)^\circ$,
 $V = 2956$ Å³, $\rho_0 = 2.15(1)$, $Z = 4$ (dimer units), $\rho_c = 2.07(20^\circ)$, $\text{MoK}\alpha$, $\lambda = 0.71069$ Å $C2/c$ (No. 15, C_{2h}^6).

Data were recorded using unfiltered $\text{MoK}\alpha$ radiation on a Syntex P1 diffractometer. The radiation was made monochromatic by using the 002

reflection from highly oriented graphite. Intensities were measured by the $\theta/2\theta$ scan technique up to a value of $2\theta = 45^\circ$. Counts were 2θ below $K_{\alpha 1}$ and above $K_{\alpha 2}$, and the background was counted on both sides. Peaks less than 3σ above the background were called unobserved, and peaks less than background were rejected. The intensity of a standard reflection was measured every 50 reflections. It showed a deviation of $\pm 2.6\%$. The linear absorption coefficient for the compound for $\text{MoK}\alpha$ radiation was 92.5 cm^{-1} . The data were corrected for Lorentz, polarization and absorption effects. The data set consisted of 1293 independent reflections of which 1087 were observed.

Solution and Refinement of the Structure

Using Patterson maps for the (100), (010) and (001) zones it was possible to detect the rhenium atoms, which occurred as centrosymmetrically related pairs. Using all the data, refinement of the rhenium atom parameters gave $R_1 = 0.23$. Electron density and difference maps located the chlorine atom and R_1 dropped to 0.18. Subsequent electron density and difference syntheses, with calculations based on known geometries for phenyl rings, revealed all the remaining atoms, except the hydrogen atoms. Further refinement, using a Cruickshank weighting scheme (33) with the weight set equal to $(75 - 0.8F_0 + 0.0029F_0^2 + 6100(\frac{\sigma}{F_0})^2)^{-1}$ for observed reflections and zero weight* for unobserved reflections, was terminated at $R_2 = 0.044$.

In all the refinement cycles of diffractometer data, which were done using the full matrix least squares programme CUDLS written for the CDC-6400 computer by J. S. Stephens, the rhenium and chlorine scattering curves of Cromer (34), including anomalous dispersion corrections (35),

* see page 81

were used. The oxygen scattering curve was also that of Cromer and that for carbon was taken from the International Tables (36). No anomalous dispersion corrections were applied to carbon or oxygen.

In the final cycle of refinement no parameter shifted by more than 1/200 of its estimated standard deviation and a series of electron density difference maps through the unit cell showed no residual peaks outside $\pm 0.8 \text{ e}/\text{\AA}^3$. The final set of atom parameters is given in Table 9 and a comparison of $|F_o|$ and $|F_c|$ is given in Appendix E.

Results and Discussion

Selected bond distances and angles are given in Table 10, and the molecule is pictured in Figure 4. The molecule is dimeric, based on the rhenium atoms, and the two halves are joined by two chlorine bridges which are symmetric. The molecule is thus very like $[\text{Re}(\text{CO})_4\text{Cl}]_2$ (44) in which two of the carbonyl groups are replaced by neutral β -ketoenol molecules bonded through the ketone groups. Surprisingly, both ketoenol groups are approximately at 90° to each of the Re-Cl bridges and are on the same side of the ReCl_2Re plane. The β -ketoenol molecules are oriented such that the best planes through the two molecules lies roughly along the Re-Cl bonds. The Re-Cl distances are $2.511(5) \text{ \AA}$ each and are comparable to the distances of $2.465(13) \text{ \AA}$ found in $\text{Re}_2\text{Cl}_{10}$ (45). The Re-O(ketone) distance of $2.16(2) \text{ \AA}$ is identical, within the errors, to the Re-O distances found in $\text{Re}_2(\text{CO})_6(\text{dbm})_2$ ($2.15(1) \text{ \AA}$) (Chapter IV) but these distances are considerably shorter than the monodentate β -ketoenolate Cu-O distance in bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)bis(NN-dimethylethylenediamine)copper(II) which is $2.76(1) \text{ \AA}$ (46). The steric requirements of the bridging chlorine atoms require the Cl-Re-Cl angle to be $80.4(1)^\circ$ ($\text{Re}_2\text{Cl}_{10} =$

81.9(4), 80.8(4)°). The C₂-Re-O(1) angle is also less than 90° (84.9(4)°). The three mutually cis carbonyl groups are possibly slightly less than 90° apart from each other (87(1), 86(1) and 88.5(9)°) and thus the angles between the carbonyl group and the chlorine and oxygen atoms are opened up from 90° (92(1) to 95(1)°).

The Re-C=O systems are essentially linear and the Re-C and C=O bond lengths are in good agreement with those found previously (Chapter IV and references therein). The β-diketone ring is essentially planar (see Table 11) and the two CO distances in the ring are significantly different at the 95% confidence level and marginally different at the 99% confidence level as are the two ring C-C distances. This suggests that the ligand is in the ketoenol form with very little, if any, delocalization of electrons, in contrast to what is found in complexes of β-ketoenolate anions. The planarity is probably maintained by hydrogen bonding from the enol oxygen atom to the ketone: the oxygen atoms are close enough (2.52(2) Å). There is probably no hydrogen bonding from the enol oxygen atom to the nearest bridging chlorine atom, as the O(OH)-Cl distance of 3.52 Å is too long (47). The least squares planes data in Table 11 also show that the phenyl group is planar, as expected and is almost coplanar with the β-ketoenol ring (dihedral angle 2.4°).

To our knowledge this is the first case where it has been clearly shown by X-ray structure determination that a neutral β-ketoenol molecule can act as a monodentate ligand, although a metal complex containing neutral acetylacetonimine has a very similar metal-ligand geometry (48). In addition such a form of bonding has been postulated in a recent paper (19) for Mn(acacH)₂Br₂. It is interesting that the

postulate by Kawaguchi et al, (19) based on infrared spectra, that metal-ligand bonding to a neutral β -ketoenolate molecule will be weaker than to the β -ketoenolate anion, and the corresponding observation by Richardson et al, (48) that M-O(ketoenolate) distances are longer than M-O(ketoenolate-hydrogen bonded) distances are not borne out for the two Re(I) compounds, $\text{Re}_2(\text{CO})_6(\text{dbm})_2$ and $\text{Re}_2\text{Cl}_2(\text{CO})_6(\text{bamH})_2$.

The packing of the molecules in the unit cell is shown in Figure 5. The molecules are packed in rows in the a direction with overlap of the β -ketoenolate and phenyl rings from alternate molecules, which are arranged head to head, like a stack of knives with blades overlapping, and the handle of each successive knife pointing in the opposite direction to the preceding one. Further contact in the a direction is between carbonyl groups in the ReCl_2Re plane. In the c direction the chains of phenyl and methyl groups contact the carbonyl groups of the next chain related by the C-centering. In the b direction the contacts are primarily β -ketoenol- β -ketoenol and carbonyl-carbonyl.

Table 9 Atomic parameters* for $\text{Re}_2(\text{CO})_6\text{C}_2(\text{bamH})_2 \times 10^3$

	x	y	z	U^{\dagger}
Re	425.14(5)	176.46(4)	327.93(6)	+
Cc	383.4(3)	188.1(2)	120.4(3)	65(1)
O(1)	441(1)	296(1)	334(1)	67(3)
C(1)	383(1)	355(1)	289(1)	59(4)
C(2)	262(1)	350(1)	199(1)	80(5)
C(3)	435(1)	425(1)	326(1)	54(4)
C(4)	541(1)	434(1)	402(1)	56(4)
O(2)	611(1)	375(1)	453(1)	76(3)
C(5)	606(1)	505(1)	444(1)	57(4)
C(6)	718(1)	506(1)	521(2)	80(5)
C(7)	778(2)	574(1)	557(2)	90(6)
C(8)	718(2)	637(1)	513(2)	93(6)
C(9)	608(2)	640(1)	438(2)	86(6)
C(10)	548(1)	571(1)	399(1)	67(5)
C(11)	429(2)	73(1)	331(2)	100(6)
O(3)	435(1)	8(1)	337(1)	129(5)
C(12)	465(1)	172(1)	486(1)	73(5)
O(4)	492(1)	174(1)	586(1)	91(3)
C(13)	280(1)	167(1)	277(1)	84(5)
O(5)	187(1)	166(1)	244(1)	125(5)

† Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	54.7(4)	62.6(5)	59.2(4)	0(10)	27.7(3)	0(4)

$^{\dagger}U$ is in $(\text{\AA})^2 \times 10^3$

* Estimated standard deviations in parentheses.

Table 10 Bond Distances and Angles $\text{Re}_2(\text{CO})_6\text{C}_2\text{H}_2$

Bonded atoms [‡]	distance Å	Bonded atoms	distance Å
Re-C ₂	2.511(5)	C(4)-O(2)	1.37(2)
Re-C ₂ *	2.511(5)	C(4)-C(5)	1.50(2)
Re-O(1)	2.16(1)	C(5)-C(6)	1.37(2)
Re-C(11)	1.87(2)	C(6)-C(7)	1.44(3)
Re-C(12)	1.86(2)	C(7)-C(8)	1.35(3)
Re-C(13)	1.85(2)	C(8)-C(9)	1.35(3)
O(1)-C(1)	1.29(2)	C(9)-C(10)	1.44(3)
C(1)-C(2)	1.49(2)	C(10)-C(5)	1.40(2)
C(1)-C(3)	1.40(2)	C(11)-O(3)	1.17(3)
C(3)-C(4)	1.32(2)	C(12)-O(4)	1.17(3)
		C(13)-O(5)	1.19(3)
Bonded atoms	angle(degrees)	Bonded atoms	angle(degrees)
C ₂ -Re-C ₂ *	80.4(1)	O(1)-C(1)-C(2)	120(1)
C ₂ -Re-O(1)	84.9(4)	O(1)-C(1)-C(3)	119(1)
C ₂ -Re-C(11)	95.4(9)	C(2)-C(1)-C(3)	121(1)
C ₂ -Re-C(12)	175.7(6)	C(1)-C(3)-C(4)	124(1)
C ₂ -Re-C(13)	95.3(7)	C(3)-C(4)-O(2)	122(1)
O(1)-Re-C(11)	173.3(9)	C(3)-C(4)-C(5)	129(1)
O(1)-Re-C(12)	92.3(7)	O(2)-C(4)-C(5)	109(1)
O(1)-Re-C(13)	109.4(7)	C(4)-C(5)-C(10)	117(1)
O(1)-Re-C ₂ *	80.0(4)	C(4)-C(5)-C(6)	123(1)
C(11)-Re-C(12)	87(1)	C(10)-C(5)-C(6)	120(1)
C(11)-Re-C(13)	86(1)	C(5)-C(6)-C(7)	121(2)
C(11)-Re-C ₂ *	93.5(9)	C(6)-C(7)-C(8)	116(2)
C(12)-Re-C(13)	88.5(9)	C(7)-C(8)-C(9)	125(2)
C(12)-Re-C ₂ *	95.9(6)	C(8)-C(9)-C(10)	118(2)
C(13)-Re-C ₂ *	175.6(7)	C(5)-C(10)-C(9)	118(1)
Re-C ₂ -Re*	98.8(1)	Re-C(11)-O(3)	177.7(6)
Re-O(1)-C(1)	141(1)	Re-C(12)-O(4)	176(2)
		Re-C(13)-O(5)	176(2)

Non-bonded atom distances: Re-Re*, 3.852(1)Å; C₂-C₂*, 3.240(5)Å; C₂*-O(2), 3.52(2)Å; C₂-O(2), 5.02(2)Å; O(1)-O(2), 2.52(2)Å.

* The superscript refers to an atom generated by (-x, y, z).

‡ Estimated standard deviations in parentheses.

Table 11 Selected Planes[‡] of Atoms in $\text{Re}_2(\text{CO})_6\text{C}_2(\text{bamH})_2$

Plane	Atoms	Deviation(Å)	Equation
A	Re	-0.06	-0.07002A + 0.99742B +0.01585C = 3.01765
	C ₂	+0.04	
	C ₂ *	-0.01	
	Re*	+0.03	
B	O(1)	+0.01	-0.65251A + 0.01914B +0.75754C = 0.31492
	C(1)	-0.01	
	C(3)	+0.01	
	C(4)	0.00	
	O(2)	-0.01	
C	C(5)	0.00	-0.62424A + 0.04314B +0.78004C = 0.76202
	C(6)	+0.01	
	C(7)	-0.01	
	C(8)	0.00	
	C(9)	+0.01	
	C(10)	-0.01	

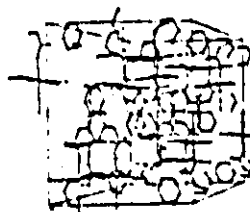
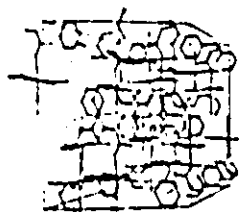
[‡] All planes are least squares planes determined by the programme PALS written by P. G. Ashmore for the CDC 6400 computer and based on the work of Schomaker et al. (49). The programme transforms the cell into an orthogonal cell corresponding to the crystallographic a, b, c* axes.

Figure 4

The molecular structure of $\text{Re}_2\text{Cl}_2(\text{CO})_6(\text{bamH})_2$. The labelling of the atoms is as in Table 9.

Figure 5

Stereogram (stereoscopic pair of perspective projections)
of $\text{Re}_2\text{Cl}_2(\text{CO})_6(\text{bamH})_2$. The c axis is parallel to the top of the page and
the b axis to the side of the page. The view is approximately along a*



CHAPTER VI

Results and Discussion

Although it was not possible to reach the original goal of this work, the preparation of $\text{Re}(\text{acac})_3$, much was learned about the reaction of $\text{Re}(\text{CO})_5\text{Cl}$ with β -ketoenols. Two types of compound were prepared when $\text{Re}(\text{CO})_5\text{Cl}$ reacted with β -ketoenols: one retained the chlorine atom and the other lost it. These were investigated in order to establish their identity.

The type which retained chlorine was shown to be diamagnetic (page 7). This suggested that the compound contained $\text{Re}(\text{I})$ and that, consequently, the β -diketone was present as a neutral β -ketoenol. The n.m.r. spectrum was also consistent with this conclusion (see later, page 49).

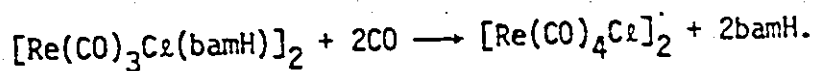
The empirical formula obtained for the benzoylacetyl methane member of the series was $\text{Re}(\text{CO})_3\text{Cl}_2\text{bamH}$. This formula would represent a normal six-coordinate species if bamH acted as a chelating ligand. However, the physical properties of the compound did not resemble those of other $\text{Re}(\text{CO})_3\text{Cl}_2\text{L}_2$ ($\text{L} = \text{py}, \text{Ph}_3\text{P}, \text{aniline}$) monomers (50,51). The low solubility and involatility suggested that the compound was a dimer or polymer, but the intractability precluded molecular weight measurements by solution or mass spectroscopic techniques.

Since we could not establish a unique structure for the compound, a single crystal X-ray analysis was undertaken to solve the problem.

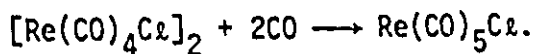
The particular compound studied here, $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{bamH})_2$, was shown by X-ray analysis to be a chlorine bridged dimer where the β -ketoenol

is monodentate and bonded to the metal via one oxygen. The bond lengths found between the atoms in the β -diketone ring also suggested that the ligand was in the ketoenol form with little, if any, delocalization of electrons, in contrast to what is found in complexes of β -ketoenolate anions. It was impossible, however, to locate the hydrogen atoms and evidence from other physical methods had to be considered, together with X-ray data, in order to eliminate alternative structures, such as a neutral β -diketone complex of Re(I) or a β -ketoenolate complex of Re(II). Mass spectroscopy of the compound was not very helpful: the compound was relatively involatile under the experimental conditions tried, and decomposed. The major peak was at m/e 162 corresponding to bamH^+ . The compound was diamagnetic and since there is a quasi-octahedral arrangement of ligands around the rhenium atom, a d^6 Re(I) system seemed more likely than a d^5 Re(II) system. The Re-Re distance of $3.852(1)\text{\AA}$ is too long to allow metal-metal bonding, although superexchange might take place through the chlorine atoms. As the compound was diamagnetic at both 23°C and -180°C any superexchange would have to be very strong.

Chemical evidence showed clearly the presence of a neutral β -diketone or ketoenol: the pure neutral ligand was isolated when our compound was treated with dry CO at 50 atmospheres in the temperature range 90°C - 150°C . The reaction is



At the higher temperature some $\text{Re}(\text{CO})_5\text{Cl}$ was obtained, probably from the reaction



Proton n.m.r. spectra gave the best evidence for the proposed structure and are consistent only with the ketoenol form. Although spectra showed that some decomposition took place with time, giving free β -ketoenol ligand, fresh solutions showed a peak at -13.8 ppm from tetramethylsilane assignable to an enol OH group and this peak was the same size as a peak at -5.55 ppm assignable to the γ C-H. (Similar peaks occur in the free ketoenol at -13.4 ppm and -5.6 ppm relative to T.M.S.)

The combination of X-ray, infrared, n.m.r. and magnetic data shows unambiguously that the structure of this compound, $\text{Re}_2(\text{CO})_6\text{C}\ell_2(\text{bamH})_2$ is correctly described here.

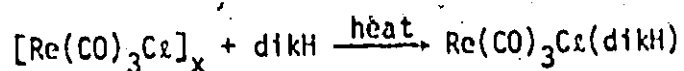
Previously, Hieber (22) assigned a structure to a complex containing a neutral (but chelated) ketoenol on the basis of a δ -OH band at $\sim 1610 \text{ cm}^{-1}$ in the infrared spectrum. Our compound also shows a band at 1610 cm^{-1} as well as two others in the $1500\text{-}1600 \text{ cm}^{-1}$ region, but our investigations of other β -ketoenolate compounds (Chapter III) show a number of complexes have three infrared absorptions in this region with the highest band, in some cases, near 1610 cm^{-1} . Thus we do not regard this as a useful diagnostic test. I have reported the infrared spectrum in detail in Chapter III. A comparison of the infrared spectrum in the carbonyl stretch region with that of $\text{py}_2\text{Re}(\text{CO})_3\text{I}$ (44) is interesting.

$\text{py}_2\text{Re}(\text{CO})_3\text{I}$	2041,	1934,	1891 cm^{-1}
$[\text{Re}(\text{CO})_3(\text{dikH})\text{C}\ell]_2$	2040,	2030,	1930, 1910, 1895 cm^{-1} .

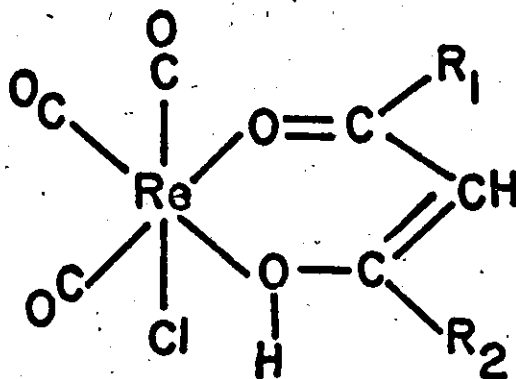
The cis arrangement of carbonyl groups postulated for the former compound

is similar to that in one half of the second compound. The extra bands are consistent with a coupling of the vibrations of the two halves of the molecule to give rise to a doubling of the 2041 cm^{-1} (2040, 2030) and 1934 cm^{-1} (1930, 1910) bands.

The work of Hieber (22) referred to above reported the preparation of the monomeric form of our compound prepared by the reaction



The structure proposed was



Very little physical evidence was given for this structure, and it seems very unlikely as we have observed no tendency for our compound to form a monomer (Chapter III page 12). If such a monomer exists, the structure of our compound, where the enol group is relatively near the bridge position, would easily allow bridge breaking. Relatively little environmental change would take place at the rhenium atom, certainly not sufficient to give rise to a drastic colour change from the

pale-yellow green of our compound to the deep red-brown of Hieber's. The final point against the structure proposed by Hieber is that, although the calculated and observed analytical results for Hieber's compounds agree very well, the calculated figures are in error and fit better a formulation $\text{Re}(\text{CO})_3\text{C}\alpha(\text{dikH})$ (see Table 12). Relatively little experimental detail is given of the preparations, but clearly this work should be reinvestigated; so far we have been unable to repeat the preparations. (Chapter III, page 13).

The second type of compound appeared to contain a β -ketoenolate anion bonded to the metal in the usual way, via the two oxygen atoms. Magnetic and infrared data were consistent with such a complex containing rhenium(I). Empirical formulas derived from the first few analyses were borderline between $\text{Re}(\text{CO})_3\text{dik}$ and $\text{Re}(\text{CO})_4\text{dik}$.

An example of the calculated values for carbon and hydrogen content for one of the first compounds in this series sent out for analysis shows the difficulty

	Calc'd	% C	% H
$[\text{Re}(\text{CO})_3\text{dbm}]_2$		43.8	2.2
$\text{Re}(\text{CO})_4\text{dbm}$		43.7	2.1

We believed the compounds were actually $\text{Re}(\text{CO})_4\text{dik}$ as we were prejudiced in favour of a six coordinate species. Early mass spectral data were confusing, however, as they showed ions only up to $\text{Re}(\text{CO})_3\text{dik}^+$. If the compounds really were $\text{Re}(\text{CO})_4\text{dik}$, then one of the carbonyl groups was excessively easy to remove under the conditions in the mass spectrometer. By varying these conditions, it was eventually possible to obtain ions

Table 12 Comparison of the Analyses of Hieber's Compounds

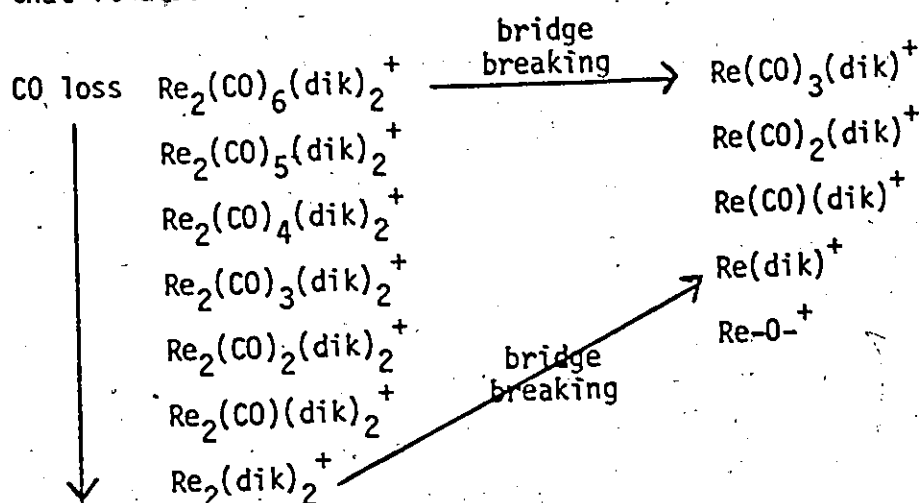
with Various Formulations

Compound	Value					M.W.
	%C	H	Re	Cl		
Acetylacetone complex (found)	25.7	1.8	43.5	8.3	429	
(C ₅ H ₈ O ₂)Re(CO) ₃ Cl (calcd.)	23.68	1.99	45.88	8.74	406	
C ₉ H ₈ ClO ₅ Re (calcd.)*	25.87	1.93	44.57	8.49	418	
(C ₅ H ₈ O ₂)Re(CO) ₄ Cl (calcd.)	25.10	1.85	42.92	8.17	434	
Benzoylacetone complex (found)	35.0	2.0	38.9	7.4	469	
(C ₁₀ H ₁₀ O ₂)Re(CO) ₃ Cl (calcd.)	33.37	2.15	39.80	7.58	468	
C ₁₄ H ₁₀ ClO ₅ Re (calcd.)*	35.04	2.10	38.80	7.38	480	
(C ₁₀ H ₁₀ O ₂)Re(CO) ₄ Cl (calcd.)	33.90	2.03	37.56	7.15	496	
Dibenzoylmethane complex (found)	42.0	2.1	34.2	6.4	561	
(C ₁₅ H ₁₂ O ₂)Re(CO) ₃ Cl (calcd.)	40.79	2.28	35.14	6.69	530	
C ₁₉ H ₁₂ ClO ₅ Re (calcd.)*	42.11	2.23	34.36	6.54	542	
(C ₁₅ H ₁₂ O ₂)Re(CO) ₄ Cl (calcd.)	40.90	2.16	33.37	6.35	558	

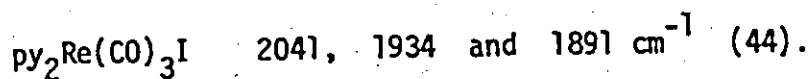
*These figures are almost identical to the figures calculated by Hieber, but which he claimed applied to the compound given on the previous line.

which corresponded not to $\text{Re}(\text{CO})_4(\text{dik})^+$, but to fragments of a dimer $\text{Re}_2(\text{dik})_2^+$. Better conditions on the mass spectrometer led to the detection of the parent ions; $\text{Re}_2(\text{CO})_6(\text{dik})_2^+$.

The mass spectra of the dimers $\text{Re}_2(\text{CO})_6(\text{dik})_2$ show a similar pattern: $\text{Re}(\text{CO})_3(\text{dik})^+$ is very abundant compared to $\text{Re}_2(\text{CO})_6(\text{dik})_2^+$. Both of the preceding ions, $\text{Re}(\text{CO})_3(\text{dik})^+$ and $\text{Re}_2(\text{CO})_6(\text{dik})_2^+$ lose carbonyls, usually one at a time, till they reach the species $\text{Re}(\text{dik})^+$ and $\text{Re}_2(\text{dik})_2^+$. The $\text{Re}_2(\text{dik})_2^+$ forms more $\text{Re}(\text{dik})$ and then this goes on to form ReO^+ compounds. The $\text{Re}_2(\text{CO})_6(\text{tfac})_2$ compound shows a variation in that it also loses F and HF.

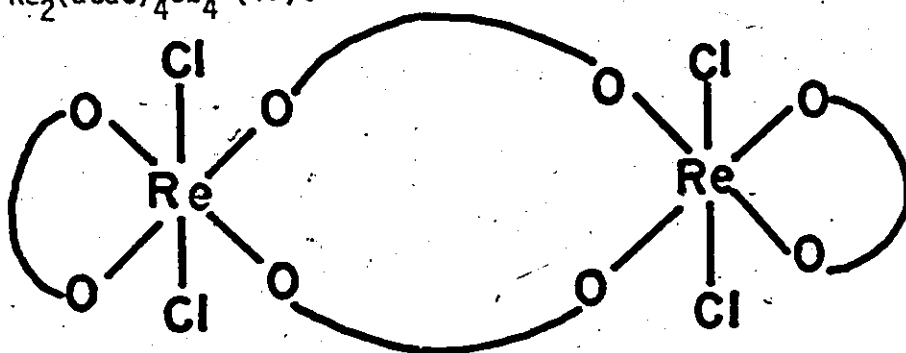


Once we discovered that we were dealing with dimers, the infrared data were re-examined to see if the type of bridging between the two halves of the dimer could be detected. An examination of the carbonyl (carbon monoxide) stretching region showed bands as low as 1890 cm^{-1} . The question arose as to whether these could be caused by bridging carbonyls. Bands near this frequency have been attributed to bridging carbonyls for other metals, but such a low value has been found for other Re(I) compounds containing only terminal carbonyl groups: e.g.



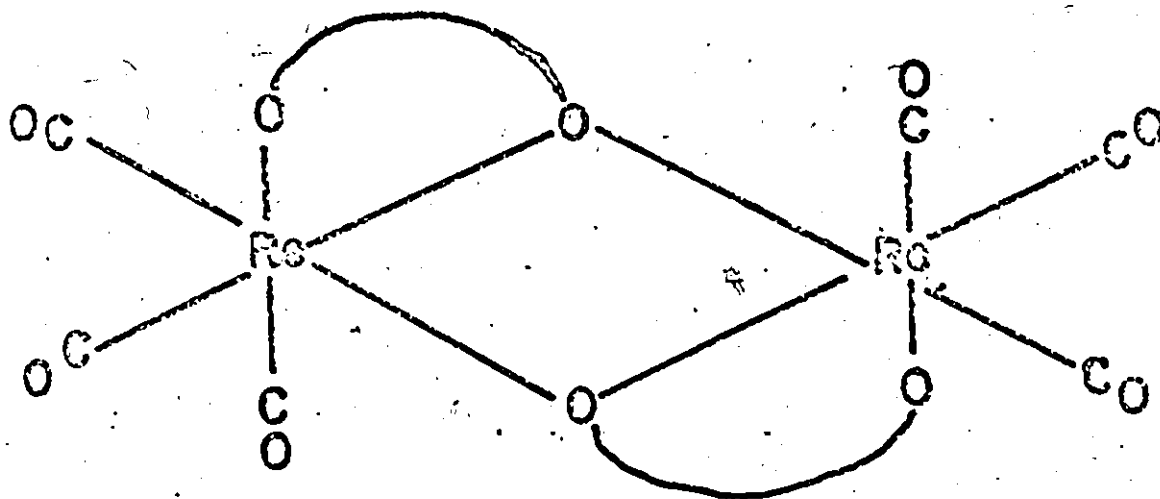
The most likely possibility, however, was that the dimer contained a weak metal-metal bond like the one in $\text{Re}_2(\text{CO})_{10}$. Such a weak metal-metal bond would explain the easy formation of $\text{Re}(\text{CO})_3(\text{dik})^+$ in the mass spectrum. Attempts to find the metal-metal bond stretch in the laser Raman spectrum near the value given for $\text{Re}_2(\text{CO})_{10}$ failed because all the samples scattered the laser beam from 0 to 200 cm^{-1} which is in the region of interest.

The second choice involved a bridge system like that postulated for $\text{Re}_2(\text{acac})_4\text{Cl}_4$ (17).

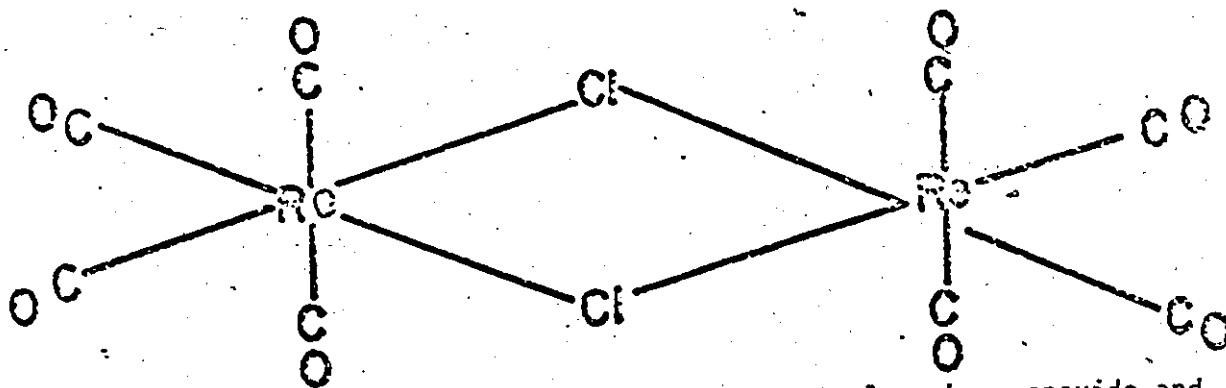


More recent work has shown that this structure is incorrect (23,24) and it, therefore, seemed unlikely for our compounds.

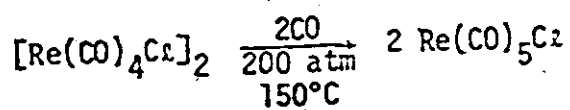
The final possibility seemed to be a bridging system similar to $[\text{Ni}(\text{acac})_2]_3$ (Fig. 1, V) (16) with one oxygen atom on each β -diketone acting as a bridge. If any of these three possibilities were correct, we would be dealing with a compound which showed novel bonding for rhenium. The structure of one member of the series $\text{Re}_2(\text{CO})_6\text{dbm}_2$ was shown to be:



Four other dimers with bridging β -diketones of this type are known (38a,b,c). One series has the formula $M_2(\text{thd})_6$ where $M = \text{Pr}$ (38c), or $M = \text{Nd}, \text{Am}$ (38b). These are very similar to our compound in that the bridge bond is perpendicular to the plane of the β -diketone. The other compound, $\text{Co}_2(\text{acac})_4(\text{H}_2\text{O})_2$ (38a), has the bridge bond in the same plane as the β -diketone ring which bridges. The structure of $\text{Re}_2(\text{CO})_6(\text{dbm})_2$ also bore a strong resemblance to that of $[\text{Re}(\text{CO})_4\text{Cl}]_2$ (44), e.g.

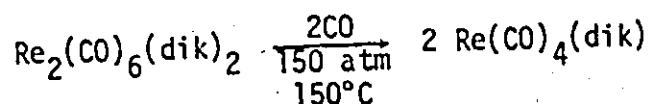


with one end of the β -diketone replacing a neutral carbon monoxide and the other end replacing a bridging chlorine. Since it is possible to carbonylate $[\text{Re}(\text{CO})_4\text{Cl}]_2$ back to $\text{Re}(\text{CO})_5\text{Cl}$ via the reaction



it seemed likely that the $\text{Re}_2(\text{CO})_6(\text{dik})_2$ series of compounds would also undergo carbonylation with a CO molecule replacing the bridge bond.

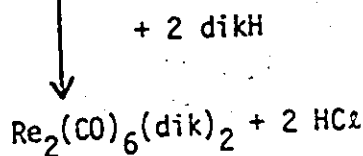
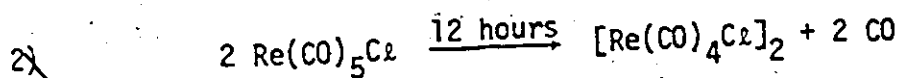
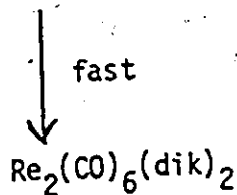
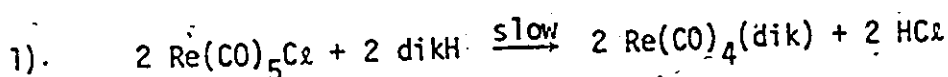
This prediction was borne out when it was found that $\text{Re}(\text{CO})_4(\text{dik})$ could indeed be formed by the following scheme



During the course of this work, the preparation of $\text{Mn}(\text{CO})_4(\text{hfac})$ from $\text{Mn}(\text{CO})_5\text{Cl}$ and hfacH was reported (6). It was interesting to compare the infrared spectrum of $\text{Mn}(\text{CO})_4(\text{hfac})$ with the spectra of the $\text{Re}(\text{CO})_4(\text{dik})$ series in the carbonyl region:

$\text{Mn}(\text{CO})_4(\text{hfac})$	2123 _w ,	2055 _s ,	1973 _s ,	1950 _s cm^{-1}
$\text{Re}(\text{CO})_4(\text{dik})$	2110 _w ,	2010 _s ,	1990 _s ,	1945 _s cm^{-1}

The question arose as to why $\text{Mn}(\text{CO})_5\text{Cl}$ gave the monomer $\text{Mn}(\text{CO})_4(\text{hfac})$ as a product while $\text{Re}(\text{CO})_5\text{Cl}$ gave the dimers $\text{Re}_2(\text{CO})_6(\text{dik})_2$. Under the reactions conditions (refluxing in benzene) two likely pathways for the reaction are:

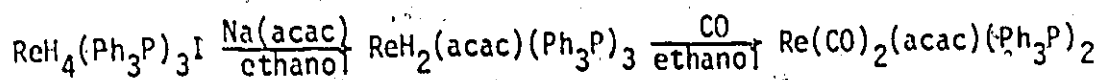


We thought that any $\text{Re}(\text{CO})_4(\text{dik})$ formed would be converted to the dimer

very rapidly in refluxing benzene. Milder reaction conditions were tried (refluxing in CH_2Cl_2 40°C) and the solutions slowly turned to the appropriate colour for the particular $\text{Re}(\text{CO})_4(\text{dik})$ compound but no product could be isolated as purification steps gave back virtually all the $\text{Re}(\text{CO})_5\text{Cl}$. The reaction was tried for a few hours in refluxing benzene with hfach as the ligand, as this β -ketoenol seemed to react the fastest. Some $\text{Re}(\text{CO})_4(\text{hfac})$ was isolated in good yield from this reaction, thus showing that the formation of $\text{Re}(\text{CO})_4(\text{dik})$ as a first step in pathway 1) (previous page) is possible. However, $\text{Re}_2(\text{CO})_6(\text{dik})_2$ compounds have been prepared directly from $[\text{Re}(\text{CO})_4\text{Cl}]_2$, thus showing that pathway 2) is also possible. The reaction to form $\text{Re}(\text{CO})_4(\text{dik})$ compounds from the dimers has been shown to be reversible by simply heating the compounds to $\sim 100^\circ\text{C}$ in air. Some even dimerize at room temperature over a period of a few months.

The resemblance of the $\text{Re}_2(\text{CO})_6(\text{dik})_2$ compounds and $[\text{Re}(\text{CO})_4\text{Cl}]_2$ can be carried further. In work reported, previous to this research (50,51), no one had ever managed to replace more than two carbonyl groups in $\text{Re}(\text{CO})_5\text{Cl}$ with donor ligands, thus giving $\text{Re}(\text{CO})_3\text{ClL}_2$ ($\text{L} = \text{py}, \text{Ph}_3\text{P}, \text{aniline}; \text{L}_2 = 1,10\text{-phenanthroline}$). (In $\text{Re}(\text{CO})_5\text{I}$, however, up to four carbonyl groups have been replaced (25a).) If a β -ketoenolate group is equivalent to one neutral carbonyl group and one chloride anion, then it should still be possible to replace two carbonyl groups in $\text{Re}(\text{CO})_4(\text{dik})$ type compounds, where the dik group has replaced one CO group and one Cl atom. Thus, we attempted to make compounds of the type $\text{Re}(\text{CO})_2(\text{dik})\text{L}_2$. Indeed, it was possible to react $\text{Re}(\text{CO})_4(\text{dik})$ and $\text{Re}_2(\text{CO})_6(\text{dik})_2$ with triphenylphosphine to obtain $\text{Re}(\text{CO})_2(\text{dik})(\text{Ph}_3\text{P})_2$ (in the case of the $\text{Re}_2(\text{CO})_6(\text{dbm})_2$ dimers,

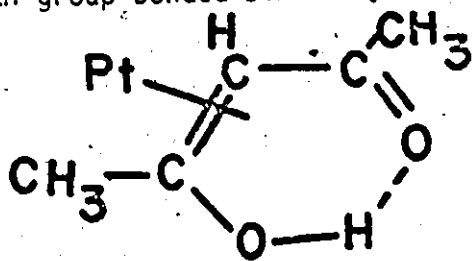
one Ph_3P breaks the bridge and the other Ph_3P replaces a carbonyl group). This was shown conclusively where the β -ketoenolate was dibenzoylmethane or trifluoroacetylacetone, and a reaction residue was obtained for acetylacetone and this residue had the same colour, solubility properties and IR spectrum as $\text{Re}(\text{CO})_2(\text{acac})(\text{Ph}_3\text{P})_2$ prepared by Freni et al. (25b) by a completely different synthetic route, e.g.



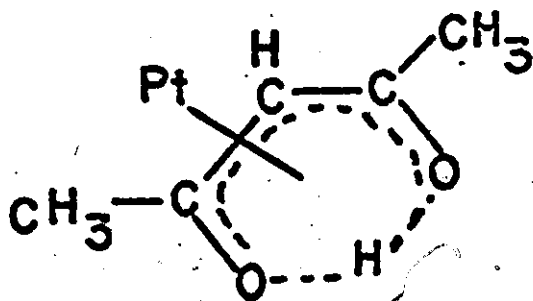
also prepared by $\text{ReH}(\text{CO})_3(\text{Ph}_3\text{P})_2 \xrightarrow{\text{acac}}$

Some monosubstituted intermediate compounds were also isolated using shorter reaction times, e.g. $\text{Re}(\text{CO})_3(\text{dik})\text{L}$ ($\text{L} = \text{Ph}_3\text{P}, \text{py}$), thus the reaction giving $\text{Re}(\text{CO})_2(\text{dik})\text{L}_2$ proceeds stepwise.

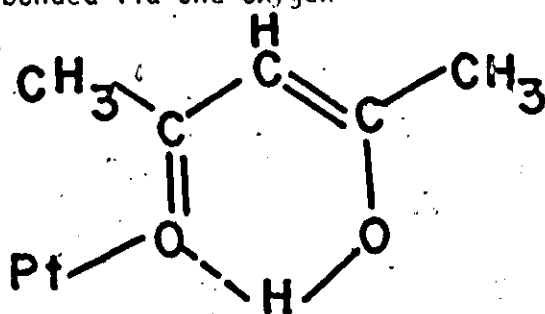
The evidence gathered from the two series of compounds reported here has shown that infrared spectra are unreliable in the prediction of these types of structures. In fact, a previously reported compound, $\text{Pt}(\text{acac})(\text{acacH})\text{Cl}$ (20,21) has been postulated from infrared and n.m.r. data to have the acacH group bonded similarly to ethylene



and was later changed to a π allyl linkage



but it is just as likely, based on our results for $\text{Re}_2(\text{CO})_6\text{Cl}(\text{bamf})_2$, that this compound is bonded via one oxygen



The bridging β -diketone groups could not be predicted from the infrared spectra either, as they appeared to be ordinarily chelated β -diketones. Our β -diketone bridged dimers and all other O-bridging β -diketones have only been detected by X-ray analysis.

CHAPTER VII

Conclusions

$\text{Re}_2(\text{CO})_{10}$ does not appear to react with β -diketones up to 373°K but $\text{Re}(\text{CO})_5\text{Cl}$ reacts to give $\text{Re}_2(\text{CO})_6(\text{dik})_2$, $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{dikH})_2$, or $\text{Re}(\text{CO})_4(\text{dik})$ and at least two reaction pathways have been shown to be possible. The $\text{Re}_2(\text{CO})_6(\text{dik})_2$ compounds can be carbonylated to give $\text{Re}(\text{CO})_4(\text{dik})$ compounds and on heating these lose carbon monoxide and reform $\text{Re}_2(\text{CO})_6(\text{dik})_2$. The $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{dikH})_2$ compounds did not react further to give the $\text{Re}_2(\text{CO})_6(\text{dik})_2$ compounds by elimination of HCl . The $\text{Re}_2(\text{CO})_6(\text{dik})_2$ and $\text{Re}(\text{CO})_4(\text{dik})$ compounds react with ligands such as pyridine and triphenylphosphine to give $\text{Re}(\text{CO})_3(\text{dik})\text{L}$ and $\text{Re}(\text{CO})_2(\text{dik})\text{L}_2$ compounds but do not react with molecular nitrogen even under pressure and at elevated temperatures. The crystal structure studies on one member of each of the series, $\text{Re}_2(\text{CO})_6(\text{dik})_2$ and $\text{Re}_2(\text{CO})_6\text{Cl}_2(\text{dikH})_2$, revealed some unusual bonding modes of β -diketones, e.g.,

- 1) a chelated β -diketone which also forms a bridge to another rhenium atom via one of the oxygen atoms and has a very large value, 37°, for the dihedral angle between the O-Re-O plane and O-C-C-C-O plane of the diketone ring.

- 2) monodentate neutral β -diketone with little or no delocalization of electrons even though the β -diketone ring remains planar.

In both the above structures, the Re-O bond length is 2.15 Å. These distances are among the longest observed for Re-O bonds. Two explanations are possible for the great length of the bond. Either one

can use Cotton's values based on the Pauling model to calculate that the Re-O bond order is 2/3; or one can argue that in these compounds, formally containing Re(I), the covalent radius is 0.11 Å longer than that calculated by Cotton for a compound of Re(V). We prefer the former interpretation. A direct comparison between the structures determined here with those of Che'ng Wan (39) (see also Chapter II) is not possible, however, since the diketones are not bonded to the rhenium atom in the same manner. Potential sources of rhenium(I) β -ketoenolates, with the β -diketone bonded in a manner similar to those of Che'ng Wan, are the monomeric compounds prepared near the end of this work, i.e., $\text{Re}(\text{CO})_4(\text{dik})$, $\text{Re}(\text{CO})_3(\text{dik})(\text{L})$ ($\text{L} = \text{py}, \text{Ph}_3\text{P}$) or $\text{Re}(\text{CO})_2(\text{dik})(\text{Ph}_3\text{P})_2$. It was also determined that the chemistry of the products was consistent with their structure.

Finally, during the course of this work, some crystals of a compound, which we have not yet identified, were isolated from the preparation of one of the $\text{Re}_2(\text{CO})_6\text{C}_2(\text{dikH})_2$ compounds. Because of the small amount of available material, the only data collected were by X-ray diffraction and the ensuing incomplete crystal structure is reported in Appendix A. The search for more of this compound may be a fruitful line of research for other workers in this field and it is hoped that the properties determined thus far will help them in their work.

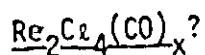
APPENDIX A

Structure of $\text{Re}_2\text{Cl}_4(\text{CO})_x$?

The work reported in this chapter is not directly related to the main part of the thesis (the reactions of $\text{Re}(\text{CO})_5\text{Cl}$ with β -ketoenols). Nevertheless, the compound described here was isolated from the reaction mixture of $\text{Re}(\text{CO})_5\text{Cl}$ and a diketone, and our initial studies assumed it was a reaction product. It now seems probable that the compound was formed during the preparation of the $\text{Re}(\text{CO})_5\text{Cl}$ starting material. Although the quantity of material was extremely limited (3 crystals, difficult to see with the naked eye $\sim 10^{-9}$ gram), a relatively large amount of information has been gathered and some conclusions can be drawn as to the nature and occurrence of this compound. The formula for the compound is followed by a question mark to indicate the uncertainty not only of the exact formula, but of some of the elements present in the compound. Although we do not know the exact preparation of this compound, we have an idea of its origin and it is useful to report the crystal structure here, since the structure may suggest a suitable preparation.

A very similar problem occurred in the case of rhenium tetrachloride in 1966 (53). Rhenium tetrachloride was prepared by accident during the commercial preparation of rhenium trichloride. Sufficient material was made to allow complete characterization and determination of the crystal structure (54,55). All attempts to repeat the preparation by the above method have been unsuccessful. The structural studies and the reported properties were useful, however, in allowing unambiguous

identification of the material, when a completely different synthetic route was found three years later in this laboratory (56). On these grounds, I feel it is useful to publish the results of this piece of incomplete work.



While searching through the flat plates of $\text{Re}_2(\text{CO})_6\text{C}_2(\text{bamH})_2$ for some more suitably shaped crystals, a few needles of the same colour were found and one was mounted along the needle axis and put on the diffractometer. Using a polaroid photograph, the Syntex diffractometer was centered on ten reflections. The derived unit cell was not the same as that obtained for the $\text{Re}_2(\text{CO})_6\text{C}_2(\text{bamH})_2$ plates but it was assumed that the two were related by a simple transformation and a set of intensity data was collected, with the idea of performing the transformation later. It soon became apparent that the unit cell of the needles could not be transformed into that of the plates and we thought that we might be dealing with another crystallographic form of $\text{Re}_2(\text{CO})_6\text{C}_2(\text{bamH})_2$.

Crystallography: The systematic extinctions of the new cell were: $h0\ell$ ($\ell = 2n+1$), $0k0$ ($k = 2n+1$) and the space group which fits this is $P2_1/c$. The cell is monoclinic with $a = 9.18(6)$, $b = 11.58(2)$, $c = 12.8(4)$ Å, $\beta = 109.1(9)^\circ$, $V = 1291$ Å³, $Z = 4$ (20°C, $\text{MoK}\alpha = .71069$ Å), $P2_1/c$ (C_{2h}^5 , No. 14).

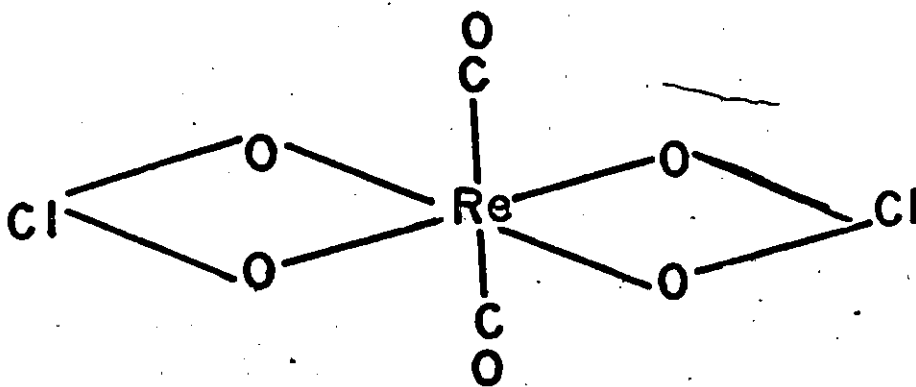
We were unable to measure the density of the compound and we have had to estimate Z . We chose $Z = 4$ on the following grounds. The calculated density for four formula units of the present known atoms per unit cell is 2.6 g cm^{-3} , which is slightly higher than other organometallic rhenium chlorides (e.g., $\text{Re}_2(\text{CO})_6\text{C}_2(\text{bamH})_2$ $d = 2.16$). A density corresponding

to $Z = 8$ would be very high (5.2 g cm^{-3}) and is only observed in very simple binary compounds of rhenium. It seemed unlikely for a complex compound. In addition, a molecular geometry calculation shows the longest adjacent atom contacts are from 3.4 to 3.9 Å away. This value is reasonable for van der Waals contact distances and implies that there are no empty spaces in the unit cell for which we have not accounted.

A total of 1623 independent reflections were measured of which 1242 were observed. The ten reflections used to center the diffractometer were used to get the unit cell parameters above.

Solution of the Structure

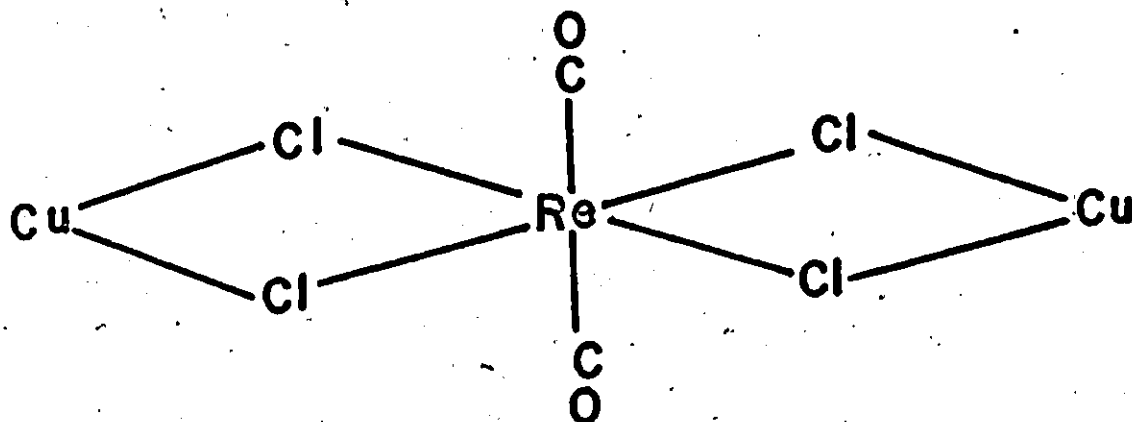
Using Patterson maps of the three zero layers, it was possible to locate what appeared to be a rhenium atom. R_2 for this trial position was .39 and the rhenium atom temperature factors were normal. An electron density and electron density difference map showed two heavy atoms which were both assigned as chlorine. The R factor dropped to .24 but the chlorine atom temperature factors were fairly large and negative. New electron density maps and difference maps using the rhenium atom and two chlorine atoms showed four symmetrically placed atoms forming a plane with the Re atom and the two Cl atoms and showed what appeared to be two carbonyl groups perpendicular to the $\text{ReCl}_2 + 4$ symmetric atom plane, with one carbonyl group on each side of the rhenium atom. A molecular geometry calculation showed the following structure:



The four symmetric atoms had been assigned as oxygen atoms. One cycle of refinement based on the above structure dropped the R factor to .20 but the temperature factors of the two chlorine atoms and four bridging oxygen atoms were fairly large and negative. This structure did not make much chemical sense, but it was decided to try and see if we could locate any (bamH) group using electron density and difference maps with the atoms in the structure just shown.

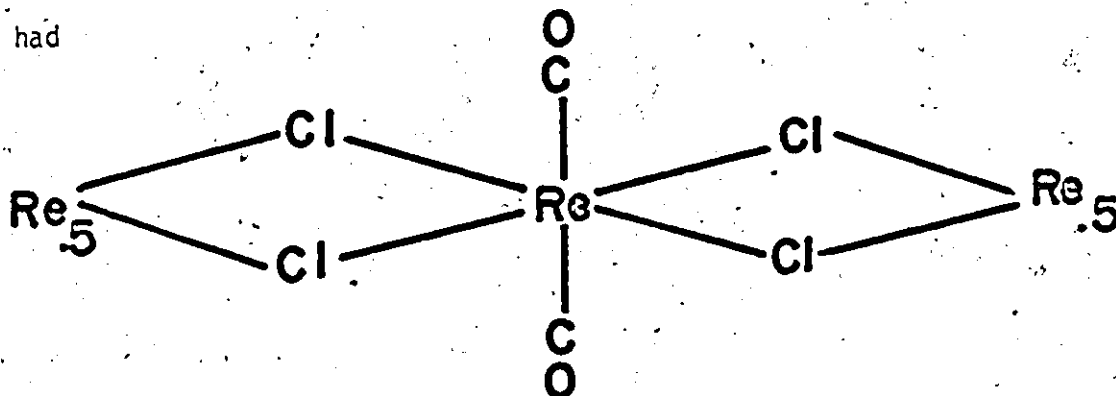
Other light atoms were located but were not stable and were not arranged in any manner resembling a (bamH) group. Further attempts also met with failure. It was decided that these green needles were perhaps some impurity and were not $\text{Re}_2(\text{CO})_6\text{Cl}(\text{bamH})_2$ after all.

The temperature factors suggested that atoms twice the size of those assigned as oxygen atoms and chlorine atoms were needed in the respective positions. The four oxygen atoms were reassigned as chlorine atoms and the two original chlorine atoms were at first reassigned as copper atoms. The copper could have carried through from the preparation of the starting material, $\text{Re}(\text{CO})_5\text{Cl}$, which is prepared from K_2ReCl_6 and copper powder under pressure of carbon monoxide. This gave the structure shown on the following page:

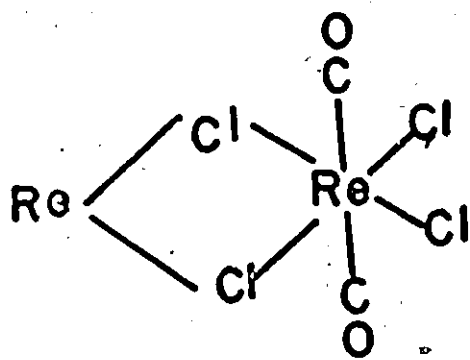


This later proved to be unsatisfactory, however, as some carbonyl groups found on the copper atoms, using absorption corrected data, seemed to form peculiar bridges from one molecule to the next. The refinement was stopped at this stage until further crystals could be found.

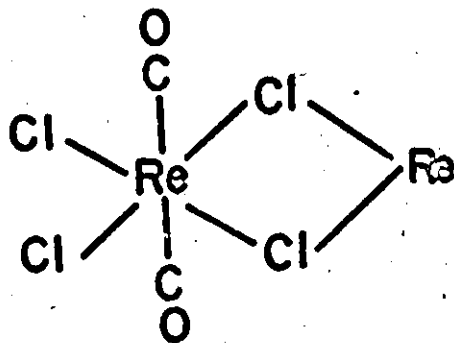
One more crystal was found, after an exhaustive search, and this was analysed on the scanning electron microprobe. The only elements found were rhenium and chlorine, with no trace of other heavy elements. Carbon and oxygen do not show up with this method. This meant that the "copper" atoms had to be accounted for in some other manner. A disordered structure was proposed where a rhenium atom with a multiplicity of .5 occurred in place of the "copper" atoms. We now had



which is really an alternation in the packing direction I and II:



I



II

There also seems to be two carbonyl groups on the disordered rhenium atom, and these are in the same plane as the rhenium and chlorine atoms, but a complete octahedral arrangement of atoms around the disordered rhenium atoms could not be found. The present trial structure is shown in Fig. 6. In all the refinement cycles, which were done using the full matrix least squares programme CUDLS written for the CDC 6400 computer by J.S. Stephens, the rhenium, and chlorine scattering curves of Cromer (34), including anomalous dispersion corrections (35) were used. The oxygen scattering curve was also that of Cromer and that for carbon was taken from the International Tables (36). No anomalous dispersion corrections were applied to carbon or oxygen.

In the final cycle of refinement, no parameter shifted by more than 1/3 of its estimated standard deviation and a series of electron density difference maps through the unit cell showed no peaks or valleys outside $\pm 3e/A^3$. The final set of atom parameters is given in Table 13 and a comparison of F_o and F_c is given at the end of this appendix. $R_1 = .16$ and $R_2 = .19$ (unit weights).

It may be argued that a discussion of bond lengths and angles

in a compound in which we are not even certain of the nature of the atoms is pointless. We have included this discussion, however, since a structure should not only make crystallographic sense, but also chemical sense. By examining the bond lengths and angles and comparing them with expected values derived from other compounds we should be able to decide whether the compound is chemical nonsense or not. It should be borne in mind in the discussion that our naming of an atom is an educated guess for the purposes of the discussion. Final proof must come later.

Results and Discussion

Selected bond distances and angles are given in Table 14 and the molecule is pictured in Fig. 6. The eight Re-C α bonds are equal (within errors) and are 2.45(3) Å on average. This bond distance is similar to that found for $\text{Re}_2(\text{CO})_6\text{C}_2(\text{bam})_2$, which also has a bridging chlorine. The four C α -Re-C α angles are also equal within errors and are 86(1)°. The four Re-C α -Re angles are 94(1)°. These angles are probably a requirement of the C α bridges as they are similar to those found for $\text{Re}_2\text{C}_2_{10}$. Perpendicular to the plane formed by all the other atoms in one molecule are two carbonyl groups, one on each side of the central rhenium atom. These are close to linear and have bond lengths similar to those outlined in Chapters IV and V.

The light atoms surrounding the disordered rhenium atoms cannot be positively identified. However, a calculation involving the volume of possible groups around the disordered rhenium atoms indicates that only small carbonyl groups or chlorine atoms could fit in the unit cell. A (bam) group would be too bulky. If enough sample

can be gathered, a neutron activation analysis (26) giving rhenium-chlorine ratios will help settle the uncertainty.




Table 13 Atomic Parameters* for $\text{Re}_2\text{C}_4(\text{CO})_x$?

Atom	x	y	z	U^\dagger
Re	.1077(3)	.1238(2)	.2255(2)	+
Re(1)**	.5207(8)	.1292(6)	.3284(7)	+
Re(2)**	.6941(1)	.1184(6)	.1218(7)	+
Ce(1)	-.101(4)	.241(3)	.249(3)	+
Ce(2)	-.096(3)	.003(2)	.097(3)	+
Ce(3)	.314(4)	.012(2)	.200(3)	+
Ce(4)	.312(4)	.244(2)	.348(4)	+
C(1)	.105(5)	.213(4)	.086(4)	0(9)
O(1)	.108(4)	.258(3)	.019(3)	15(9)
C(2)	.107(6)	.458(5)	.859(5)	11(12)
C(3)**	.33(1)	.54(1)	.197(9)	12(24)
O(3)**	.25(1)	.025(9)	.708(8)	33(24)
C(4)**	.346(9)	.717(7)	.078(7)	0(17)
O(4)**	.29(1)	.809(9)	.004(9)	42(26)

† Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	11(1)	1(1)	37(2)	0(1)	2(1)	0(1)
Re(1)	37(3)	25(4)	82(6)	0(3)	11(4)	0(4)
Re(2)	33(3)	28(4)	84(6)	0(3)	11(3)	0(4)
Ce(1)	93(18)	64(18)	111(26)	0(15)	4(17)	0(17)
Ce(2)	41(11)	43(13)	166(31)	16(10)	35(15)	28(17)
Ce(3)	85(21)	57(17)	107(26)	0(15)	0(18)	0(16)
Ce(4)	101(22)	44(15)	198(38)	53(15)	73(24)	46(19)

Estimated standard deviations in parentheses.

$^\dagger U$ is in $\text{\AA}^2 \times 10^{-3}$.

**These atoms have a multiplicity of .5.

Table 14 Selected Bond Distances* and Angles* for $\text{Re}_2\text{C}_4(\text{CO})_8$

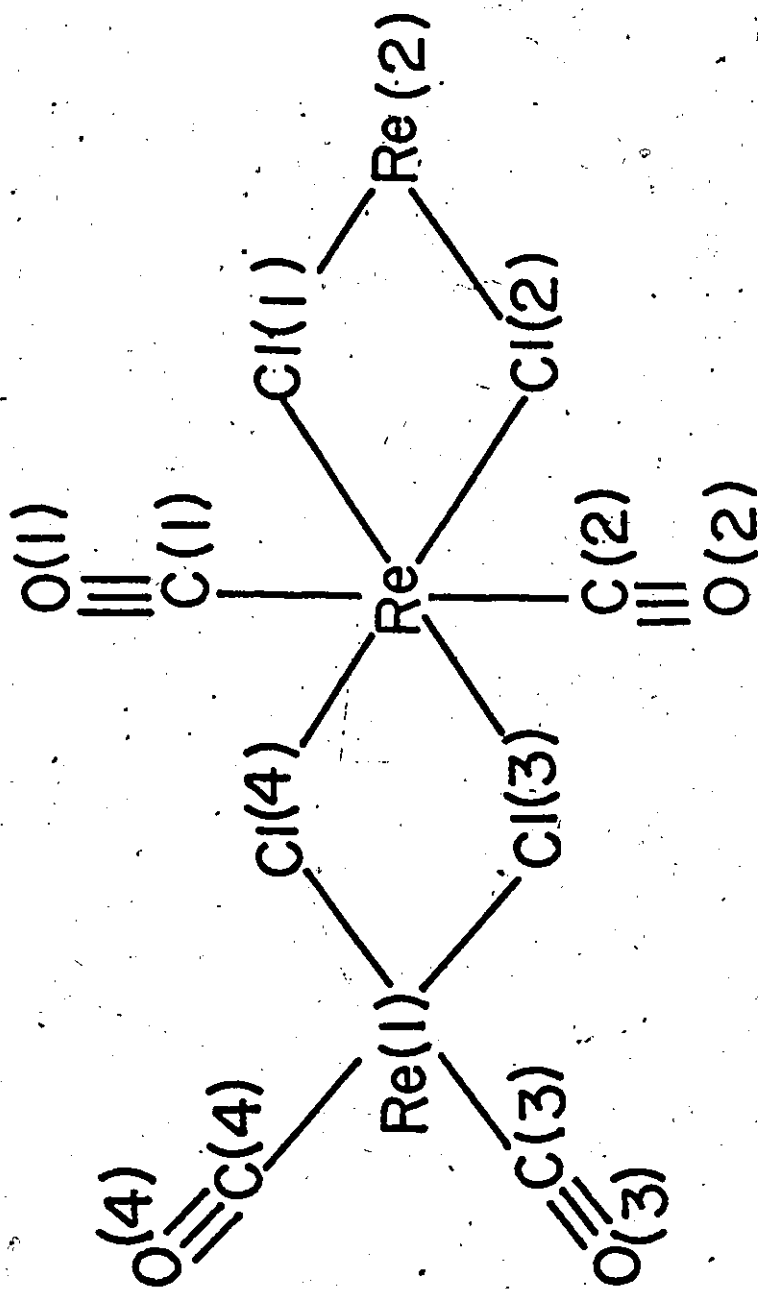
Bonded atoms	distance (Å)	Bonded atoms	distance (Å)
Re -C ϵ (1)	2.45(4)	Re(1)-C(3)	1.80(1)
Re -C ϵ (2)	2.48(3)	Re(2)-C ϵ (1)	2.50(3)
Re -C ϵ (3)	2.40(3)	Re(2)-C ϵ (2)	2.45(3)
Re -C ϵ (4)	2.45(3)	Re(1)-C(4)	1.73(7)
Re -C(1)	2.06(5)	C(1) -O(1)	1.02(7)
Re -C(2)	1.97(6)	C(2) -O(2)	1.19(8)
Re(1)-C ϵ (3)	2.48(3)	C(3) -O(3)	1.1(2)
Re(1)-C ϵ (4) ϕ	2.42(4)	C(4) -O(4)	1.4(1)

Bonded atoms	angle (deg)	Bonded atoms	angle (deg)
C ϵ (1)-Re -C ϵ (2)	87(1)	Re -C ϵ (1)-Re(2)	93(1)
C ϵ (1)-Re -C ϵ (3)	179(1)	Re -C ϵ (2)-Re(2)	93(1)
C ϵ (1)-Re -C(1)	92(1)	Re -C ϵ (3)-Re(1)	94(1)
C ϵ (1)-Re -C(2)	86(2)	Re -C ϵ (4)-Re(1)	95(1)
C ϵ (3)-Re -C ϵ (4)	86(1)	Re -C(1) -O(1)	178(3)
C(1) -Re -C(2)	178(2)	Re -C(2) -O(2)	178(3)
C ϵ (3)-Re(1)-C ϵ (4)	85(1)	Re(1)-C(3) -O(3)	171(12)
C ϵ (1)-Re(2)-C ϵ (2)	87(1)	Re(1)-C(4) -O(4)	157(7)

* Estimated standard deviations in parentheses.

Figure 6

Molecular structure of $\text{Re}_2\text{Ce}_4(\text{CO})_x$?



APPENDIX B

X-ray Diffraction

Introduction

Groups of atoms usually pack into crystals in such a way that the same atoms repeat themselves at regular intervals in three dimensions. The volume of space which is unique and is repeated by simple translation in space is known as the unit cell and is defined by a , b , c , α , β and γ where a , b and c are the three sides defining the limits of the unit cell, α is the angle between b and c ; β between a and c ; and γ between a and b .

Since the spacing between the atoms is of the same order of magnitude as the wavelength of the X-rays, the X-rays are diffracted and can be made to produce spots on a film. The size of the unit cell determines, via an angular function, the distance between reflections, and the number of electrons (and therefore atoms) interacting with the X-ray beam, as well as the relative arrangement of the atoms, determines the intensities of the reflections. Only those reflections which undergo constructive interference will show up. This condition is met when (57) the incident and diffracted beams are coplanar with the normal to a crystal lattice plane and the angle from the plane of the incident and diffracted beams are the same. This may be expressed as Bragg's law

$$n\lambda = 2d\sin\theta$$

where d is the distance between two adjacent parallel planes, θ is the

angle between the plane and the incident and diffracted beam, λ is the wavelength of the X-rays and n is an integer called the order of reflection. The lattice planes are numbered using integers h , k and l which are called Miller indices and are defined such that any hkl plane, which contain the origin, intersects a at a/h , b at b/k and c at c/l .

Structure factors

The electrons in the atoms scatter the X-rays. Waves scattered by different atoms generally differ in phase because of the difference in path length of the two X-rays. In some arbitrary direction defined by the vector \vec{H} , the result of these waves may be summed up to give the structure factor $F_{\vec{H}}$

$$F_{\vec{H}} = \sum_{j=1}^N T_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

where f_j is the atomic form factor (scattering factor) of the j^{th} atom and is a Fourier transform of the electron density, $\rho(x,y,z)$, x_j , y_j , and z_j are the fractional coordinates of the j^{th} atom along a , b and c , respectively. T_j is the temperature dependent term and is

$$T_j = \exp(-B_j \frac{\sin^2 \theta}{\lambda^2})$$

where B_j is a Debye-Waller temperature factor (58, 59) and accounts for the thermal motion of the atoms from their average position.

In general, the structure factor F is expressed in two parts:

$$F = A + iB$$

where

$$A = \sum_{j=1}^N f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

and
$$B = \sum_{j=1}^N f_j \sin 2\pi(hx_j + ky_j + lz_j)$$

so that $FF^* = A^2 + B^2$. The phase angle of F , $\alpha = \tan^{-1} B/A$ is not an observable quantity and only the intensities FF^* can be obtained. These are corrected for Lorentz (L) (60), polarization (P) (60) and absorption (A^*) (60) such that the intensity I is

$$I = k |F_0|^2 (A^*)^{-1} L \cdot P$$

where k is a scale constant. A^* depends on size of crystal and its contents,

$$P = \frac{1 + \cos^2 2\theta}{2}$$

L depends on technique used.

Patterson functions

Since the phases are not known, the electron density cannot be found directly. For the structures solved in this thesis, the rhenium atoms were found using the Patterson function. Correct positions for the rhenium atoms usually sets enough phases for the other atoms to be found from electron density maps. The Patterson function is

$$P(u, v, w) = V \int_0^1 \int_0^1 \int_0^1 \rho(x, y, z) \rho(x+u, y+v, z+w) dx dy dz$$

Using structure factors this is

$$P(u, v, w) = \frac{1}{V} \frac{\sum_{k\ell} |F_H^*|^2 \cos 2\pi(hu + kv + \ell z)}{\sum_{k\ell} 1}$$

Usually, information from the 3 zero layers was used independently to get

two dimensional projections. In the Patterson function there are maxima corresponding to each interatomic vector

$$\vec{V} = \vec{V}_i - \vec{V}_j$$

where $\vec{V}_i = (x_i\vec{a} + y_i\vec{b} + z_i\vec{c})$ is the position of an atom in the unit cell. There are N atoms in a unit, each with z_i electrons ($i = 1, 2, \dots, N$); this will create N^2 maxima in the Patterson function of height $z_i z_j$. N of these occur at the origin and $N(N-1)$ occur elsewhere; but most peaks blend into a common background except the rhenium-rhenium interactions which, because of the large number of electrons relative to the usual other atoms, stand out above the background.

The rhenium atom positions were then tried alone as a trial structure and the rhenium atoms usually set a large number of phases so that lighter atoms could be found from electron density (61) and difference Fourier maps.

Least-squares refinement

The set of structure factors, $|F_c|$, calculated from the proposed model are then compared to the observed structure factors ($|F_o|$). The correctness of the structure is tested by comparing the $|F_o|$ and $|F_c|$ in two conventional functions-

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_2 = \left[\frac{\sum \omega ||F_o| - |F_c||^2}{\sum \omega F_o^2} \right]^{1/2}$$

R_1 is called the unweighted R factor and R_2 is called the weighted R

factor. The weighting scheme used in this work is called a Cruickshank (33) weighting scheme. It gives slightly more weight to medium intensity data which are more likely to contain accurate information on the positions of the lighter carbon and oxygen atoms; very intense reflections contain mainly data on rhenium positions and very weak reflections may have a high relative error. The expression for Cruickshank weights* is

$$w = (A + BF_0 + CF_0^2)^{-1}$$

where A is approximately the lowest F_0 which is observed, B is close to -1 and C is about $1 \div$ the highest F_0 . (This gives only order of magnitude approximations.)

If F_c is expressed as a linear function of the parameters x_i by using a Taylor expansion then the sum of the squares of the discrepancies between the real and trial x_i 's can be minimized using Legendre's principle (62) in a program such as CUDLS written by Dr. J.S. Stephens for the CDC 6400.

* This weight, multiplied by .9, is also given to unobserved reflections which have a higher F_{calc} than the F_{obs} .

APPENDIX C

Abbreviations Used in the Text

Ligands:

- L - monodentate ligand
dikH - neutral β -ketoenol
dik - β -diketonate anion
acac - pentane-2,4-dionate anion
hfac - 1,1,1,5,5,5-hexafluoropentane-2,4-dionate anion
dbm - 1,3-diphenylpropane-1,3-dionate anion
tfac - 1,1,1-trifluoropentane-2,4-dionate anion
ttfa - 1,1,1-trifluoro-3-thenoylacetate anion
tfba - 4,4,4-trifluoro-1-phenyl-1,3-butanedionate anion
bamH - 1-phenyl-1,3-butanedione
thd - 2,2,6,6-tetramethyl-3,5-heptanedionate anion
py - pyridine
Ph - phenyl

Infrared Spectroscopy:

- vs - very strong
s - strong
ms - medium strong
m - medium
mw - medium weak
w - weak
vw - very weak
sh - shoulder

APPENDIX D

Observed and Calculated Structure Factors for $\text{Re}_2(\text{CO})_6(\text{dbm})_2$.

*ALUE = 0 = OBSERVED REFLECTION
ALUE = 1 = UNOBSERVED REFLECTION

ALUE

F (OBS)

F (CALC)

KLUE

F (OBS)

F (CALC)

ALUE

F (CALC)

9

APPENDIX E

Observed and Calculated Structure Factors for $\text{Re}_2(\text{CO})_6\text{C}_2(\text{bpmH})_2$.

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