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ABSTRACT

The current work focused on the preparation of organometallic derivatives of rhenium metal carbonyl complexes. The ligand derivatives were prepared as precursors to the metal carbonyl complex target species.

The ligands that were coordinated to the metal carbonyl moeity are triphenylphosphine and trimethylphosphine. These ligands were prepared by a microscale Grignard synthesis beginning from readily available starting reagents. The purity and characterization of these ligands were performed by FT-IR spectroscopy.

The derivatives were coordinated to the metal carbonyl moeities by allowing the two species to react in refluxing bis-(2-methoxyethyl)ether and triethanolamine solvents. The reactions required a minimum of six hours, on the microscale, in order to ensure completion. The former solvent was chosen for coordination of triphenylphosphine; and the latter for coordination of trimethylphosphine. The resulting rhenium carbonyl products were characterized by FT-IR spectroscopy.

Carbonyl stretching frequencies for many compounds containing strongly π-accepting ligands give characteristic absorption bands in the 2000 cm^{-1} region. These stretching frequencies often yield real Cotton-Kraihanzel force constants if the two physically different cis-CO-CO interactions are differentiated [1].

PREPARATION AND CHARACTERIZATION OF CARBONYLTETRAKIS(TRIMETHYLPHOSPHINE)RHENIUM(I)CHLORIDE

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PREFACE

Bonding in metal carbonyls is currently of interest. A molecular orbital description can be employed to interpret the vibrational spectra of a number of metal carbonyls. An important factor in this description is the extent of the presence of the carbon monoxide π^* orbitals in the electron filled molecular orbitals of the metal carbonyl moeity. The π^* participation increases substantially in the isoelectronic series - $Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^=$, as the atomic number of the metal atom decreases [2]. A consideration of the Hartree-Fock terms in the molecular orbital secular equation suggests that this will also happen in a given metal carbonyl moeity as the negative charge on it is increased [3].

The interest in these tertiary alkyl phosphine derivatives of rhenium carbonyl complexes can also be attributed to the fact that certain of these complexes can actually function as effective catalysts for the homogeneous hydrogenation of a variety of unsaturated substances. Previous work with the rhodium complex, dichlorotris(triphenylphosphine)rhodium(II), indicated that it dissociated in benzene solution to give coordinatively unsaturated species [4]. Thus, these authors thought that the rhenium complex should behave similarly. A detailed study of the rhenium complex with various solvents and solvent mixtures would necessarily determine the extent of hydrogenation and if an induction period was required before hydrogenation occurs. The authors apparently thought that the solvent has an effect upon the extent of hydrogenation of the complex.

Speculation on the use of these complexes as co-polymers and cross-linking adducts in certain types of polymerization reactions has provided insight into a new class of polymeric materials of ultra-high tensile strength and ductility. These complexes, once formed, are surprisingly stable to air, light, and water. In fact, even when exposed to direct sun-light over the course of several months, they only darken slightly [5].

In addition to the proposed use of these metal complexes as co-polymers in polymerization reactions and catalysts in homogeneous hydrogenation reactions, the mechanisms of ligand exchange in these transition metal complexes are of interest. In general, exchange reactions may occur either by 1) unimolecular,dissociative S_N1 type processes or by 2) bimolecular, displacement S_N2 type processes. Ligand substitutions in octahedral metal(III) complexes apparently occur by both S_N1 and S_N2 mechanisms. This phenonomenon is supported by stereochemical and kinetic evidence as presented by Ingold, Nyholm, and co-workers [5]. The mode of exchange depends upon the nature of the ligands on the metal, the nucleophilicity of the attacking species, and the solvent. As a result of the investigation of the alkaline hydrolysis of metal(III) octahedral complexes, a dissociative S_N1CB (substitution, nucleophilic, unimolecular, conjugate base) mechanism was proposed, in which the intermediate is the pentacoordinated metal atom [7].

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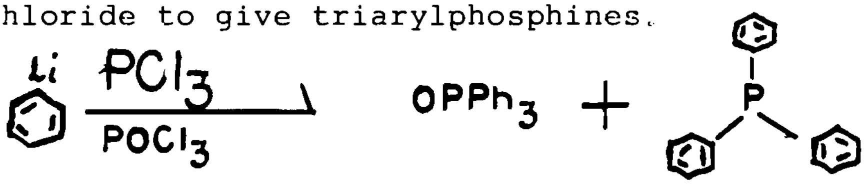
I. HISTORICAL

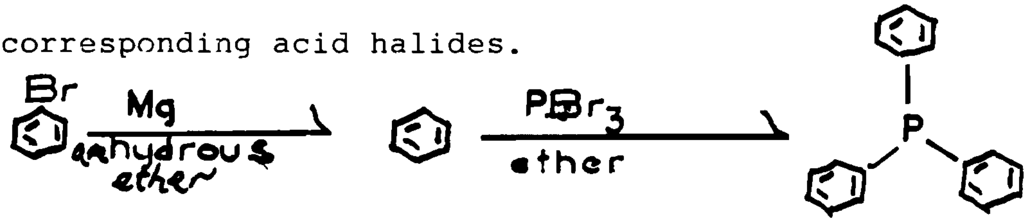
A. Preparation of Tertiary Aryl Phosphines

Mikhailov and Kucherova [8] condensed aryllithium derivatives with phosphorus trichloride and phosphorus oxychloride to give triarylphosphines.

(1) 

The yield of phosphines appeared to be substantially improved when phenyllithium was caused to react with various esters of phosphorus, phosphoric acid, and dialkylphosphochloridates.

The alkyllithium synthetic route was one of the variety of methods used for the production of tertiary phosphines. Other methods include the reaction of Grignard reagents with triesters of phosphoric acid or the corresponding acid halides.

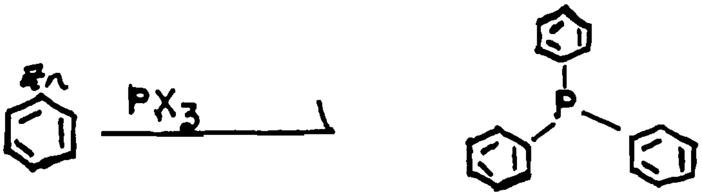
(2) 

Tertiary aryl phosphines can also be prepared by the reactions of: [9]

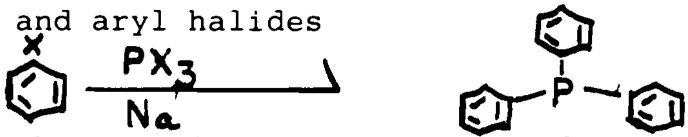
a) metallic phosphides with alkyl halides

$$MgPH_2 \xrightarrow{RX} PPh_3$$

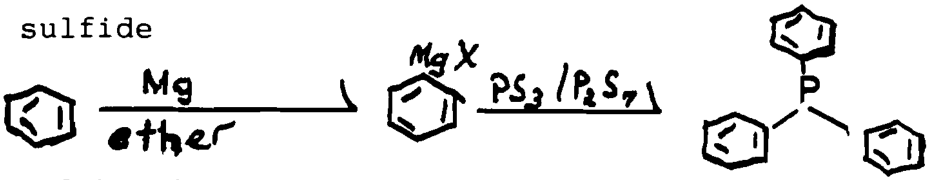
b) the condensation of organozinc reagents with phosphorus trihalides



c) the Wurtz reaction between phosphorus halides and aryl halides



d) the reaction between Grignard reagents and phosphorus trisulfide or phosphorus heptasulfide



Triphenylphosphine was initially prepared, in the laboratory, by Dodonov and Medox [10] in 1928. Triphenylphosphine was prepared in 76% yield from phenylmagnesium bromide and phosphorus trichloride in anhydrous diethyl ether under a H_2 atmosphere with constant cooling. It was determined that when a diethyl ether solution of the compound was treated with phenylmagnesium bromide in diethyl ether and a current of oxygen was blown through the cooled mixture for 1.5 hrs., tetraphenylphosphonium bromide was obtained.

Triarylphosphines and triacylphosphines have also been prepared in non-ethereal media by Zakharkin, Okhlobystin, and Strunin [11]. Their method involved the use of ether-free Grignard reagents for the preparation of organometallic compounds. A brief description of the synthetic route is as follows: Magnesium shavings are activated with crystalline iodine, followed by the addition of bromobenzene in dodecane. The mixture was held at reflux for one hour and at a still-pot temperature of 160 °C. After this, the mixture was treated with phosphorus tribromide and heated for an additional three hours. After filtration, the triphenylphosphine was isolated in a 75.3% yield with a boiling point of 165 °C and a melting point of 80 °C.

The yields of the Grignard products were determined by the double-titration method, which is described as follows:

1. Double-Titration Method

The resulting solution is filtered under an atmosphere of dry nitrogen. An aliquot (5-10 mL) of this solution is hydrolyzed in 10 mL of distilled water. Titration with standard acid, such as 6 M HCl, using phenolphthalein as indicator, gives the total alkali. A second 5-10 mL aliquot is added to 10 mL of dry ether containing 1 mL of benzyl chloride (purified by drying over phosphorus pentoxide, P_2O_5, and then distilling at reduced pressure). As the arylmagnesium is delivered, a yellow-color flashes through the liquid. If the R-Mg is concentrated, a white precipitate of magnesium chloride forms with the disappearance of the yellow-color. (The aqueous layer decolorizes before the ether layer near the endpoint). Overshooting the endpoint can be eliminated by vigorous swirling near the endpoint. (Note: Ether is the best solvent to use as coupling of the R-Mg with the benzyl chloride takes place much less readily in other solvents.)

The molecular weights of the magnesium compounds were determined using a Washburn and Read apparatus [12]. Following up on the preparation of tertiary phosphines, one can speculate on the formation of tertiary phosphine oxides, sulfides, and selenides [13].

Tertiary phosphine oxides can be prepared from the tertiary phosphines by conversion into the oxide by means of oxygen, nitric acid, nitrous oxide, chromic acid, potassium chlorate, and peroxides.

(3) $$PPh_3 \xrightarrow{HNO_3/KClO_3} Ph_3PO$$

Another method involves the addition of a halogen to the phosphine followed by the hydrolysis of the tertiary phosphine dihalide.

(4) $$PPh_3 \xrightarrow{X_2} Ph_2PX_2 \xrightarrow{H_2O/OH^-} Ph_3PO$$

Grignard and organozinc reagents may react with the halides or esters of phosphorus acids to give tertiary phosphine oxides, and such products may also be the result of the thermal decomposition of quaternary phosphonium hydroxides, alkoxides, and the Arbuzov rearrangement of dialkylphosphinates.

(5)

$$(EtO)_3P \longrightarrow (EtO)_2\overset{O}{\overset{\|}{P}}CH_2R$$

Tertiary phosphine sulfides have been produced in similar ways [14]; however thiophosphorylchloride has been shown to react in a surprising fashion with Grignard reagents [15]. This reaction produces a tetra-substituted bis-phosphine disulfide.

(6) $$SPOCl \xrightarrow{RMgX} Ph_2PS_2$$

Tertiary phosphine selenides have also been prepared by the addition of selenium to the corresponding phosphine [14].

(7) $$PPh_3 \xrightarrow{Se} Ph_2PSe$$

In a similar fashion, then, the general method for the preparation of triphenylphosphine can be used for the preparation of trimethylphosphine, one of the precursors enroute to the synthesis of the target molecule carbonyltetrakis(trimethylphosphine)rhenium(I) chloride.

(8) $$CH_3Cl \xrightarrow[\text{dry ether / THF}]{Mg} CH_3MgCl \xrightarrow{PCl_3} CH_3PCl_2 \longrightarrow (CH_3)_3P$$

The substitution of alkyl groups for halogens continues until all available halogens have been replaced by alkyls, as depicted in the above equation. However, it is possible to stop the reaction before all of the halogens have been replaced.

B. Preparation of Trimethylphosphine

A number of methods by which to prepare tertiary alkyl phosphines are apparent. One method that affords excellent yields of tertiary alkyl phosphines involves the alkylation of dialkylhalophosphines with organic lead compounds [16]. The alkylation can be done stepwise, making it possible to prepare tertiary phosphines containing three different organic groups.

Kharasch et.al. [16] showed that tetraethyllead reacts with phosphorus trichloride to yield ethyldichlorophosphine. Dialkylchlorophosphines are produced, with further alkylation, at higher temperatures [17]. Dialkylhalophosphines then react further, by a stepwise process, to form tertiary phosphines:

(9)

$$3\,PCl_3 \xrightarrow{PbR_4} 3\,RPCl_2 + PbCl_2 + RCl$$

(10)

$$RPCl_2 \xrightarrow{PbR'_4} RR'PCl + PbCl_2 + R'Cl$$

(11)

$$RRPCl \xrightarrow{PbR''_4} RR'R''P + PbCl_2 + R''Cl$$

Upon heating at higher temperatures for longer time intervals similar exchange reactions were observed for quadruply connected phosphorus halogen compounds, where X = (O,S) [16]:

(12)

$$3PXCl_3 \xrightarrow{PbR_4} 3RPXCl_2 + PbCl_2 + RCl$$

(13)

$$3RPXCl_2 \xrightarrow{PbR'_4} 3RR'PXCl + PbCl_2 + R'Cl$$

(14)

$$3RR'PXCl \xrightarrow{PbR''_4} 3RR'R''PX + PbCl_2 + R''Cl$$

The reaction is catalyzed by aluminum trichloride. The phosphonyl halides react much more slowly than the sulfur containing species, and only with much longer heating periods. Phosphorus thiotrichloride, when used in excess with organolead and tin compounds, gave appreciable amounts of the dialkylated product, thiophosphinic halide [18]. A possible explanation may be that thiophosphinic halides are alkylated about as fast as phosphorus thiotrichloride. The reactivities of phosphorus and organolead compounds were analyzed by ^{31}P NMR with the following results:

a) Reactivity of phosphorus compounds

$PBr_3 \approx CH_3PBr_2 > PCl_3 > CH_3PCl_2 \approx C_6H_5PCl_2 >$
$(CH_3)_2PCl \approx (C_6H_5)_2PCl > PSCl_3 \approx C_6H_5PSCl_2 \approx$
$CH_3PSCl_2 > ClCH_2PSCl_2 > (CH_3)_2PSCl > POCl_3 \approx$
$C_6H_5POCl > ClCH_2POCl_2$

b) Reactivity of organolead compounds

$Pb(CH_3)_4 \approx Pb(C_2H_5)_4 > Pb(C_4H_9)_4 > Pb(C_6H_5)_4$

C. Some Chemistry of Rhenium

The intent of this section is to focus on the chemistry of the element rhenium and its most favorable coordinating ligands. Some pertinent background information concerning the elements' origin and preparation will be discussed. This information will be effectively utilized to provide an approach to the coordination of metallic rhenium and complexation with carbon monoxide.

The proposed synthesis of the carbonyl compound, carbonyltetrakis(trimethylphosphine)rhenium(I)-chloride will be postulated and assessed according to feasibility and cost effectiveness. The proposed synthesis will be adapted to the microscale.

Rhenium lies within Group VII B of the Periodic Table, along with technetium and manganese. Although rhenium was not discovered until 1925, its chemistry has been widely investigated [19]. Each of the elements in Group VII B is characterized by valence electrons in two shells, the outermost one of which contains two electrons. Thus, one would expect similar chemical properties for the metals in this group, along with similar trends in bonding and compound formation. When these metals are contrasted with the halogens (Group VII A), one can deduce that the halogens are active non-metals (seven electrons in valence shell) whereas the Group VII B elements are active metals. In the higher oxidation states, striking similarities exist between the two groups. For example, potassium perrhenate and potassium perchlorate are both strong oxidizing agents that form isomorphous crystals of similar solubilities [20].

Like other metals of the second and third transition series, rhenium in most of its compounds and complexes has low spin; also the halides produce only poorly defined and ill-characterized species in solution. For rhenium, the +3, +4, and +7 states are the most common; although the +2 and +1 species are formed under suitable conditions. Except for carbonyls and carbonyl derivatives, which are similar to manganese, rhenium resembles both molybdenum and platinum in its chemistry [21].

The oxy anion, ReO_4^-, is well known in aqueous solution. Polarographic studies of the reduction of this anion in aqueous solution containing supporting electrolytes with various anions have been done, but although potential values can be associated with the observed reduction steps, the precise nature of the species present is obscure [22].

D. Preparation of Rhenium Metal

Although rheniums' existence was predicted much earlier from the periodic table, it was first detected by X-ray crystallographic analysis in 1925. Several prior attempts to isolate the element failed primarily due to its low abundance (1 X 10^{-9}%) in the earth's crust [23]. The discoverers, Noddack and Tacke, later isolated about a gram of rhenium from molybdenite [24].

Rhenium is now recovered from the flue dusts in the roasting of molybdenum sulfide ores and from residues in the smelting of some copper ores. The element usually remains in oxidized solutions as the perrhenate ion, ReO_4^- [25]. After concentration, the perrhenate is precipitated, by the addition of KCl, as the sparingly soluble salt, $KReO_4$. Rhenium metal can then be obtained by the hydrogen reduction of this salt, but is best obtained by the thermal decomposition in hydrogen of NH_4ReO_4 [26]. Fine NH_4ReO_4 powder is slowly heated to 200-250 °C in very pure hydrogen and held at that temperature for three hours. The temperature is then raised to 500 °C and the reduction completed at 1050 °C for six hours.

If heating rates are too high, part of the product evaporates as the oxide and deposits to form a mirror on the walls of the reaction vessel.

$KReO_4$, in a silver boat, is reduced in very pure hydrogen at 500 °C. The product is extracted with water containing a small amount of HCl, dried, and again reduced with hydrogen at 1000 °C in a porcelain boat [27].

1. Properties [23]

The metal resembles platinum in appearance but is usually obtained as a grey powder. It crystallizes in the hexagonal close-packed arrangement and burns in oxygen upon heating to 400 °C, to give the oxide Re_2O_7 which sublimes away. In moist air the metal is slowly oxidized to the oxy acids. Rhenium is soluble in warm bromine water, but is insoluble in hydrofluoric and hydrochloric acids. Rhenium is also soluble in hydrogen peroxide.

At the present time rhenium metal is not widely used and the alloys suffer from their reactivity toward oxygen; however with inert gas protection a very useful Pt-Re thermocouple can be prepared.

2. <u>Compound Formation</u> [28]

Rhenium forms oxide compounds and most importantly, heptoxides by combustion of the metal in oxygen.

The isomorphous sulfides, ReS_2, Re_2S_7 are known. The black heptasulfides are obtained by saturation of 2-6 $\underline{N}$ HCl solution of ReO_4^- with H_2S. The precipitation is sensitive to conditions and is often incomplete. The treatment of neutral solutions of oxy anions with thioacetamide or sodium thiosulfate followed by acidification gives a better yield. Excess sulfur in the precipitates may be extracted with carbon disulfide. The rhenium disulfides are obtained by heating the heptasulfides in vacuum. These compounds have a tendency to be nonstoichiometric.

Rhenium forms several fluorides. The most common, ReF_6 is obtained by direct interaction of the elements at 120 °C; it is a low-melting solid with a high vapor pressure at 25 °C. Spectroscopic studies have shown that it possesses an octahedral structure. The compound is very moisture sensitive and gives ReO_2, $HReO_4$, and HF on hydrolysis. Other fluorides are possible and are formed, such as: ReF_7, ReF_5, and ReF_4.

Upon heating rhenium metal in oxygen-free chlorine, the hexachloride is obtained as a green vapor which condenses to a green-brown solid. Other chlorides such as $ReCl_5$ and Re_2Cl_6 are possible [20].

Rhenium also forms a series of stable complex hexahalo anions, such as ReX_6^{2-}, and complex cyanides, as $Re(CN)_8^{2-}$.

Complex formation of rhenium with oxygen, nitrogen, phosphine, arsine, sulfur, and carbon monoxide are also possible. Chelating disulfides give species such as: $(CH_3S(CH_2)_2SCH_3)ReCl_3$. Dithiocarbamate complexes such as: $(C_2H_5NHCS_2)ReCl_2$ also have been prepared [29].

In 1937, Lundell and Knowles [20] found that when acid perrhenate solutions are reduced with zinc amalgam in a Jones reductor, a reduced rhenium species is obtained which has a formal oxidation state of -1. They considered this reduced species to be the "rhenide" ion, Re^-. Thus, complexes with Re-H bonds can be obtained fairly readily. Those exist mostly in the hydrate form, $Re(OH_2)^-$.

As was mentioned previously, rhenium forms coordination complexes with carbon monoxide known as rhenium carbonyls [30]. Like most metal carbonyls, rhenium carbonyls have the general formula $Re_x(CO)_y$ and can be categorized according to the following molecular formulas: 1) $Re(CO)_4$, 2) $Re(CO)_5$, 3) $Re(CO)_6$, 4) $Re_2(CO)_{10}$, 5) $Re_2(CO)_9$, 6) $Re_2(CO)_8$, 7) $Re_3(CO)_{12}$, 8) $Re_4(CO)_{12}$, and 9) $Re_6(CO)_{16}$.

The internal bonding has been considered to consist of the following three types: a) Covalent metal-metal bonds, are described as each metal donating one electron; b) Coordinate-covalent carbon-metal sigma-type bonds, with the carbon atom donating a pair of electrons to the metal and receiving a partial π-type "backbonding" from the d-electrons of the metal; and c) Covalent metal-carbon sigma-type bonds, with the carbon atom acting as a bridge between the two metal atoms resulting in bond formation. Recent X-ray analysis suggests that the complex, $Re_6(CO)_{16}$ possesses bonding involving metal-carbon monoxide bonds in which the carbon atom serves as a bridge between three metal atoms [31].

Most of the metal carbonyls have demonstrated the utility of the Sidgwick rule regarding the effective atomic numbers (E.A.N.) of the transition metals involved [29]. This rule suggests that each metal should react in a manner so as to acquire the same number of external electrons as the corresponding noble gas. Metals with uneven atomic numbers form carbonyls that utilize metal to metal bonds, or bridging carbonyls, or display the paramagnetic effects associated with unpaired electrons.

3. Carbonyl Halides of Rhenium

$Re(CO)_5X$ and $Re(CO)_4X_2$ can be prepared by action of the halogens on the rhenium carbonyl [32]. Carbonyl chlorides can also be prepared. This can be effectively accomplished by allowing a solution of the corresponding metal carbonyl to react with carbon tetrachloride at 25 °C. The thermal stability of these carbonyls decreases from left to right across the Periodic Table.

Metal carbonyls can be characterized spectroscopically [32]. A monosubstituted carbonyl $LM(CO)_5$ has C_{4v} symmetry. The vibrations can be classified by symmetry rules, as E (allowed, x-y polarized), 2A (allowed, z-polarized), and B_1 (forbidden). The E vibration corresponds to the T_{1u} vibrational mode of the hexacarbonyl and should account for 4/5 of the total intensity of absorption. The two A_1 vibrations are comprised of the stretching mode of the unique carbonyl and the breathing mode of the other four. If the two A_1 motions did not couple, the stretching mode would be allowed, accounting for the remaining 1/5 of the total intensity, while the breathing mode would be essentially forbidden (although it could have a small intensity due to non-coplanarity of the radial carbonyl groups and to electronic migrations along the four-fold axis accompanying the symmetrical stretching of the carbonyls). In the two A_1 modes interaction occurs and some of the intensity of the one strongly absorbed must be transferred to the other. Thus, one would expect one very strong band and two or three much weaker bands. The sign of the interaction constant between carbonyl groups places the weak A_1 band at a higher frequency than the E band. An analogy with carbonyls suggests that for rhenium compounds there should be an interval of 100-120 cm^{-1} between bands.

Trans dicarbonyls give rise to an antisymmetric B_1 stretching mode corresponding to one component of the T_{1u} mode and an essentially forbidden A_1 mode.

The cis dicarbonyls show two bands of comparable strength. In symmetrical C_{3v} tricarbonyls two bands are expected - a degenerate one of lower frequency having roughly twice the intensity of the second band due to the non-degenerate A_1 vibration. In unsymmetrical tricarbonyls there should be a pair of bands separated by 100 cm^{-1} and one further moderately strong band due to the unique carbonyl group.

In most carbonyl compounds, trans pairs of carbonyl groups have stronger C-O force constants than carbonyl groups cis to substituents. This leads to a very characteristic spectrum consisting of a number of intense carbonyl bands separated by 100 cm^{-1} from a weak high frequency band. This feature also seems to occur in certain five-coordinate carbonyls, but in an octahedral complex it is diagnostic of a pair of trans carbonyls in a molecule of relatively low symmetry.

For trans pairs of carbonyl groups in rhenium compounds the characteristic separation between strong and weak bands lies in the region 115 cm^{-1}.

In many alkyl and acyl substituted rhenium compounds a large number of extra bands appear. In some cases as many as six carbonyl frequencies are seen. These are attributed to the occurrence of Fermi resonance or the presence of isomeric impurities.

Even though the acyl group lacks approximate axial symmetry, acyl metal carbonyls probably contain a symmetry plane including the R-CO-M group. This should lead to a small and possible resolvable splitting of the intense E transition, and to the appearance of the B transition with low intensity. The occurrence of a single weak extra band between the E and higher frequency A_1 bands can be ascertained [33].

Tertiary phosphine complexes of the type, $Re_2Cl_4(PR_3)_4$ have been prepared from the reaction of the $Re_2Cl_6^{2-}$ anion with the corresponding phosphine [34]. Single-crystal X-ray structure analysis has shown that the phosphine species possesses a strong rhenium-rhenium quadruple bond.

Dinuclear rhenium(III) species contain a quadruple bond [34]. Structurally and electronically similar compounds are formed by technetium, ruthenium, tungsten, chromium, and molybdenum. The "Scattered-Wave-$X\alpha$" method has been used to calculate ground-state electronic spectra and optical spectra of the octachlorodirhenate(III) species [35]. It is not clear whether the electronic structures of reduction products can be predicted by the addition of one or two electrons to the LUMO's of these species. This procedure would result in the population of the δ^* orbital by one or two electrons. This should partially or totally nullify the δ-bond and abolish whatever structural features are attributable solely to the presence of the δ-bond.

A stable compound, $Re_2Cl_4(PEt_3)_4$, can be prepared by reaction of PEt_3 with either Re_3Cl_9 or salts of the $Re_2Cl_8^-$ anion [36]. The molecular structure was found to have the following features: 1) trans-$ReCl_2(PEt_3)_2$ halves joined by a Re-Re bond; 2) the halves are in an eclipsed rotational relationship about the Re-Re bond; 3) point group symmetry, D_{2d}; 4) Re-Re bond length 2.232 Å which differs significantly from the bond lengths in compounds of rhenium(III) in which there are quadruple bonds, $Re_2Cl_8^{2-}$ (2.222 Å) and $Re_2Cl_6(PEt_3)_2$ (2.222 Å); and 5) crystallizes in the space group Im3m with a = 12.345 Å and z = 2.

$Re_2Cl_4(PEt_3)_4$ is a symmetrical molecule with two electrons outside of the $\sigma^2\pi^4\delta^2$ configuration [37] (see Figure 1).

The formula units in the cubic space group, Im3m, would have to lie at positions (0,0,0) and ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and have crystallographic symmetry m3m, a requirement obviously inconsistent with the stoichiometry for an ordered structure [35]. The mode of disordering was deduced to be that in which the dumbbell-shaped Re_2 units are randomly oriented along the x,y,z axes defining an octahedral set of metal atoms. The chlorine and phosphorus atoms are randomly disordered over the centers of the octahedral faces [38]. Anisotropic refinement of the rhenium units (110 reflections with $|F_o| > 3\sigma(F_o|)$ of the 1/3Re, $\frac{1}{2}$Cl, $\frac{1}{2}$P, and $\frac{1}{2}$C atoms converged to residuals of $R_1 = 0.041$, and $R_2 = 0.052$.) It is suggested that occupation of the δ^* orbital in this sterically crowded molecule is unlikely in view of the similarity of the Re-Re bond length to those in species where the δ^* orbital is recognized to be unoccupied [39].

Ground state configurations of d^5-d^5 systems of $Re_2Cl_4(PPh_3)_4$ are on the order of $\sigma^2 \pi^4 \delta^2 \delta^{*2}$ with state symmetry A_1. The ground state configuration for the d^5-d^4 $Re_2Cl_4(PPh_3)_4^+$ system is $\sigma^2 \pi^4 \delta^2 \delta^*$ with A_2 state symmetry [37]. As a consequence for both systems the many electron wave function can be represented by a single Slater determinant, and the total energy evaluated by the corresponding statistical energy expression used in connection with the Hartree-Fock-Slater method. The d^4-d^4 $Re_2Cl_4(PPh_3)_4^{2+}$ system has the ground state configuration $\sigma^2 \pi^4 \delta^2$ with state symmetry A_1 [40].

The δ overlaps between the two d_{xy} orbitals are small, so that the energy separation between δ and δ^* is modest. The configuration $\sigma^2\pi^4\delta^{*2}$, as well as the ground state configuration, can be represented for many electron wave functions, d^4-d^4, by two Slater determinants as:

$$\Psi = c_1|\sigma^+\sigma^+\pi_1^+\pi_1^-\pi_2^+\pi_2^-\delta^+\delta^-| + c_2|\sigma^+\sigma^+\pi_1^+\pi_1^-\pi_2^+\pi_2^-\delta^{*+}\delta^{*-}|$$

Thus, it can be summarized that the most compelling criterion for the existence of a metal-metal bond is the metal-metal bond distance. The length of a bond of a given multiplicity between a given pair of metal atoms is a sensitive function of a variety of parameters, including oxidation states, nature of additional ligands, and other aspects of molecular structure.

E. Carbonyl Derivatives of Tertiary Aryl and Tertiary Alkyl Phosphine Complexes of Rhenium(II) and Rhenium(III)

The discovery of multiple bonds between transition metal atoms, in the early 1960's, led to an exploration for understanding the chemistry of triply and quadruply bonded species of rhenium [41]. The structural characterization of compounds of rhenium of this type and theoretical advances (especially SCF-$X\alpha$-SW calculations), coupled with detailed spectroscopic studies, have generated an understanding of the electronic structures of these species [42,43].

Investigations into two aspects of their chemical reactivity have been attempted. One explored the redox chemistry of low oxidation state metal-metal bonded dimers. These dimers possess electronic configurations of the type $(\sigma)^{2}(\pi)^{4}(\delta)^{a}(\delta)^{*b}(\pi)^{*0}(\sigma)^{*0}$, where a = 1 or 2 and b = 0-2. The object was to develop a reversible four electron oxidant-reductant which retains its structural integrity [37,44]. The other use of these "coordinatively unsaturated" dimers was as synthetic intermediates, particularly in reactions where disruption of the strong metal-metal bond occurs [45].

A study of the reactions of CO with the complex $Re_2Cl_4(PEt_3)_4$, an example of a molecule which possesses a Re-Re triple bond and a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration, led to the possibility of synthesizing the complex $Re_2Cl_4(PEt_3)_4(CO)_2$ along with species in which substitution of the Cl^- or PEt_3 ligands might occur without disruption of the metal-metal bond [37]. The object was to determine what effect the π-acceptor CO ligands had upon both the Re-Re bond length and molecular geometry of the complex $Re_2Cl_4(PEt_3)_4(CO)_2$. It was found that this reaction was extraordinarily complicated giving rise to products arising from both the cleavage of the Re-Re triple bond and the oxidation of the Re_2^{4+} core. Analogous reactions were found to occur with other complexes of the type $Re_2X_4(PR_3)_4$. These provide a route to the paramagnetic rhenium(II) complexes $ReX_2(CO)_2(PR_3)_2$.

F. Carbonylation Reactions of $Re_2X_4(PR_3)_4$ [37]

The reactions between CO and $Re_2X_4(PR_3)_4$ in refluxing ethanol, toluene, or acetonitrile are extremely complex and lead to the formation of mixtures of $Re_2X_2(CO)_2(PR_3)_2$, $ReX(CO)_3(PR_3)_2$, $Re_2Cl_5(PR_3)_3$, $Re_2Cl_6(PR_3)_2$, and trans-$ReCl_4(PR_3)_2$. The product distribution depends upon the starting material, the choice of solvent, and the reaction time.

Reactions of CO with $Re_2X_4(PR_3)_4$ in refluxing ethanol for periods of less than 3 hrs. afforded complexes of the type, $ReX_2(CO)_2(PR_3)_2$. Other products isolated from the same reaction mixture were of the type, $ReX(CO)_3(PR_3)_2$ [46].

Extending the reaction time to 12 hrs. or more resulted in the disappearance of $ReX_2(CO)_2(PR_3)_2$ and $Re_2Cl_5(PR_3)_3$, and increased the yield of $ReCl(CO)_3(PR_3)_2$, and when using toluene as solvent, the appearance of higher oxidation state species, trans-$ReX_4(PR_3)_2$ and $Re_2Cl_6(PR_3)_2$. In all cases, X = Cl or Br, and R = Et or n-Pr.

1. Properties and Structure of $ReX_2(CO)_2(PR_3)_2$

This complex is soluble in a variety of polar and non-polar solvents, is a monomer in benzene, and possesses a room-temperature magnetic moment of 2.1 μ_B. This value is consistent with its formulation as a derivative of rhenium(II) (T_{2g}^5 configuration). The solid-state room-temperature ESR spectrum of $ReX_2(CO)_2(PR_3)_2$, where again X = Cl or Br, and R = Et or n-Pr, is broad (fwhm $\approx$ 450 G) and centered at a g_{av} value of 2.25. The proton NMR spectrum in $CDCl_3$ consists of one broad band which is centered around δ = 1.6 ppm. The Me_4Si signal is also very broad, a consequence of the paramagnetic nature of the complex. This is further evidence for the complex being a rhenium(II) $T_{2g}{}^5$ species, since paramagnetic rhenium(III) $T_{2g}{}^4$ complexes have sharp resonances which are shifted relative to those of their diamagnetic analogues [46].

The infrared spectrum of $ReX_2(CO)_2(PR_3)_2$ is in accord with a trans disposition of both Re-CO and Re-Cl bonds, possessing both single ν(CO) and ν(Re-Cl) absorptions (see Table I). Accordingly, it most likely has an all-trans geometry, similar to that exhibited by certain ruthenium(II) complexes of this type [47].

G. Relationship Between the Reactivities of Rhenium Dimers Containing Metal-Metal Triple and Quadruple Bonds

Most reactions of the octahalodirhenate(III) anions, species which possess a Re-Re quadruple bond and a $\sigma^2 \pi^4 \delta^2$ ground state electronic configuration, [41] occur with retention of the metal-metal bond although under certain circumstances this bond may break, as in its photochemical cleavage [48]. Upon ultraviolet irradiation of acetonitrile solutions of $(Bu_4N)_2Re_2Cl_8$, photochemical cleavage of the metal-metal bond occurs.

An interaction between $Re_2X_8^{2-}$ (or $Re_2X_6(PR_3)_2$) and various ligands is that involving a non-sterically hindered π-acceptor ligand such as CO. This type of interaction might weaken the Re-Re bond so that it eventually dissociates. This type of π-acceptor ligand may compete with the electrons used in the Re-Re π-bonding (d_{xz}-d_{xz} and d_{yz}-d_{yz}) overlaps thereby weakening the metal-metal bonding. However, no such reaction occurs when $Re_2X_6(PR_3)_2$ is treated with CO in refluxing ethanol [49]. However, it was observed that the rhenium(II) dimers which possess the same molecular structures as their molybdenum(II) analogues but different electronic structures (triple vs. quadruple metal-metal bonds) react very rapidly with CO to produce $ReX_2(CO)_2(PR_3)_2$. This difference in reactivity is probably a consequence of differences in the electronic structure of the M_2^{n+} units and is not associated directly with variations in the ligand sets since isoelectronic $Re_2X_6(PR_3)_2$ and $Mo_2X_4(PR_3)_4$ have different combinations of Cl^- and PR_3 ligands, yet neither reacts with CO. It is possible that in $Re_2X_4(PR_3)_4$, overlap between the anti-bonding orbitals of π symmetry on CO and the metal-based π-bonding molecular orbitals is now more favored compared to the situation with $Re_2X_6(PR_3)_2$ and $Mo_2X_4(PR_3)_2$, thereby leading to an intermediate such as $Re_2X_4(CO)_2(PR_3)_4$ which contains terminal CO groups collinear with the Re-Re bond. The coordination of these π-acceptor CO ligands may so weaken the Re-Re bond that the metal centers become susceptible to further nucleophilic attack by CO to form a second intermediate, containing both terminal and bridging CO groups. This second intermediate would be an 18-electron metal-metal bonded dimer, but severe steric crowding about the eight-coordinate metal atoms would likely favor its conversion to the dicarbonyl monomer (see Figure 2).

H. Preparation of Rhenium(III) Chloride as Precursor Enroute to the Synthesis of $ReCl_2(CO)_2(PPh_3)_2$

$$(15)\quad Re_{(s)} + 3/2\ Cl_{2(g)} \longrightarrow ReCl_{3(s)}$$

Rhenium metal is placed in a reactor consisting of a quartz tube joined to a receiver manifold to which are sealed seven bulbs [20]. The air is displaced with oxygen-free N_2 and the rhenium is heated in a continuous stream of Cl_2. The sublimate is collected in the first bulb and then resublimed into the second bulb. The operation is repeated with the next set of bulbs. The fractions are collected and resublimed at 2-3 mm and 550 °C.

1. Properties

The compound forms dark, purple-red crystals with a hexagonal structure. It is bimolecular under normal conditions, Re_2Cl_6, and is converted in moist air to $ReCl_3 \cdot 3H_2O$. The waters of hydration are readily removed by heating to 100 °C, under vacuum, over P_2O_5. The anhydrous chloride, $ReCl_3$ is soluble in water with a deep, dark-red color; the solution turns cloudy after several hours due to incomplete hydrolysis, and black $Re_2O_3 \cdot H_2O$ is precipitated. The $Re_2O_3 \cdot H_2O$ is completely hydrolyzed upon boiling the solution. This compound is soluble in acetic acid, dioxane, ethanol, NH_4OH, and is slightly soluble in diethyl ether. Addition of an aqueous $AgNO_3$ solution produces a precipitate only after lengthy heating with nitric acid. The anhydrous chloride forms well crystallized compounds with RbCl, CsCl, and organic bases ($R-NH_2$).

II. EXPERIMENTAL

A. General Experimental Reagents and Conditions

1. ACS certified-grade chemicals

Baker and Adamson Products, Specialty Chemicals Division, Allied Chemical Corp.

Magnesium metal turnings; Sodium sulfate, anhydrous

Matheson, Coleman, Bell, Inc.

Benzene

Fisher Scientific

Calcium chloride, anhydrous (4-20 mesh); Iodine, resublimed; Sodium chloride; Sodium hydroxide, pellets; Isopropanol; Petroleum ether; N,N-dimethylformamide; Methanol; Toluene; Chloroform; Acetone; Potassium iodide; Ammonium chloride; Methyl iodide

2. ACS reagent-grade chemicals

Fisher Scientific

Diethyl Ether, anhydrous; Carbon tetrachloride; Triethanolamine

Mallinckrodt Chemical

Carbon disulfide

Matheson, Coleman, Bell, Inc.

Phosphorus tribromide

3. ACS purified-grade chemicals

Fisher Scientific

Bromobenzene

4. ACS practical-grade chemicals

   Eastman Kodak, Organic Chemicals Division

     Bis-(2-methoxyethyl)ether

   Commercial Solvents Corp.

     Dibutyl ether

5. ACS HPLC-grade chemicals

   Fisher Scientific

     n-hexane

6. Miscellaneous chemicals

   Midwest Grain Products

     Absolute ethanol, 95% w/w

   Anachemia Chemical Company

     Accutint^{R} indicator paper (pH range 1-12)

   Alfa Chemicals

     Rhenium(III) chloride, anhydrous (99% purity)

   Iowa Beef Processing Co., Emporia, Kansas

     Dry ice (solid CO_2)

   Brown Welding Supply, Salina, Kansas

     Compressed nitrogen gas

Microscale Organic Qualitative Labware, purchased as a ChemKit^{R} from Wheaton Scientific, was routinely employed to perform the desired chemical syntheses.

Dibutyl ether was dried, overnight, in contact with calcium chloride at 80 °C. It was then distilled under reduced pressure (110 °C, 1 mm).

All of the syntheses in this research were carried out on the microscale in a glove bag under an atmosphere of dry nitrogen. The glove bag was charged with dry nitrogen to a pressure of 748 mm. The nitrogen flow-rate was monitored at 1.0 mL/min by means of a paraffin-oil bubble-chamber.

The gravimetric analyses of the rhenium complexes were performed according to the following method [49].

Carbon monoxide from metal carbonyls can be converted to hydrogen and carbon dioxide by a convenient modification of the water gas shift (WGS) reaction. This is effectively accomplished in homogeneous systems with liquid water present.

Following dissociation of the CO moeity from the metal carbonyl, the carbon monoxide is passed directly into liquid water. As a result, the CO is converted to CO_2 via an in situ shift. The carbon dioxide thus generated is then absorbed into soda-lime for quantitative assay.

The chlororhenium tertiary phosphine complex was then distilled over and absorbed into a saturated potassium iodide solution that was 1.1 $\underline{M}$ in silver iodide. The tertiary phosphine precipitated as the tertiary phosphine-silver iodide complex which was then weighed.

Tetraphenylarsonium chloride was regenerated from the hydrate by heating under reduced pressure for one hour (80 °C, 1 mm).

The rhenium chloride product was then heated at reflux (80 °C) with 1.0 $\underline{M}$ $(C_6H_5)_4AsCl$ solution, in a still pot equipped with a Claisen distillation head and condenser, for one hour. The evolved chlorine was condensed into a 1.0 M solution of orthotoluidine. The orthochlorotoluidine solution was then evaporated to dryness and the resulting yellow crystals of orthochlorotoluidine weighed.

The still pot mixture was then allowed to cool to room temperature, followed by further cooling in an ice bath. The rhenium was precipitated as the tetraphenylarsonium perrhenate salt which was dried in vacuo (100 °C, 1 mm) for six hours. This salt was then weighed and the percent rhenium in the rhenium carbonyl complex determined.

The FT-IR spectrophotometric analyses for each of the compounds prepared in the research were performed according to the following conditions.

Spectra were scanned on a Bomem^R Model MB-100 FT-FT-IR spectrophotometer equipped with KBr optics, using 4 cm^{-1} resolution, and KBr salt plates. The spectra were scanned from 5000 cm^{-1} - 1000 cm^{-1}. The interferograms and spectra were processed with Spectra-Calc^R software and a NEC APV IV microprocesser, Model 109PO912W4031, equipped with an EGA color monitor. The KBr salt plates were from Wilmad Glass Works, Spectra-Calc^R software was from Galactic Industries, Inc., and demountable salt plate cells were from McCarthy. Teflon spacers of 55-45μ thickness were used to obtain solution spectra.

The following syntheses are modifications of the procedures as described by Dodonov and Medox [10] and C. Tegner [50] and scaled to fit microscale apparatus.

B. Preparation of Phenylmagnesium Bromide

Magnesium metal turnings (18 mg, 0.075 mol) were placed in a 5.0 mL reaction vessel with 200 μL of anhydrous diethyl ether (dried over $CaCl_2$) and activated with crystalline iodine.

An aliquot (76 μL, 0.075 mmol) of bromobenzene in 400 μL of diethyl ether was gradually introduced into the reaction vessel via a 1.0 μL syringe over a 3-5 minute interval with continuous stirring and dry nitrogen flow.

Upon completion of the reaction, 300 μL of diethyl ether were added, in a single step, and the ether was maintained at steady reflux for 15 minutes at 50-60 °C.

C. Preparation of Triphenylphosphine

The above reaction mixture was then cooled to 15 °C using a slurry of sodium chloride and crushed ice. Next a solution of phosphorus tribromide (37 μL, 380 μmol) in 400 μL of diethyl ether was added dropwise to the cooled phenylmagnesium bromide reaction mixture. The addition of the phosphorus tribromide was complete after thirty minutes. Upon completion of the addition of phosphorus tribromide, 300 μL of diethyl ether were added, in a single step, and the mixture heated to reflux for 1-2 hrs. Upon cooling, the mixture was hydrolyzed with an excess of 10% sodium hydroxide solution until the aqueous layer tested alkaline with Accutint^R indicator paper. The ether layer was then separated from the aqueous layer via pipette technique, and the aqueous layer treated with three 0.5 mL aliquots of ether. Each of the three ether extracts were combined with the original ether layer.

The ether layer was dried over anhydrous sodium sulfate for 24 hrs. and then transferred to a weighed Craig recrystallization tube for solvent evaporation. Yellow-white crystals of triphenylphosphine resulted. The crude triphenylphosphine was sublimed in vacuo at 80 °C and 0.75 mm pressure. Pure, white crystals of triphenylphosphine were collected, recrystallized twice from a mixture of isopropanol and petroleum ether (1:1) and once from ice-cold absolute ethanol. The white needles weighed 48 mg with a melting range of 75.0-79.0 °C. The molecular weight was ascertained by an ebullioscopic procedure as 259.3 g/mol.
(Calculated: 262.0 g/mol) [Note: The ebullioscopic determination of the molecular weight was performed with the boiling point elevation of benzene, $\Delta T_{bp} = K_{bp}m$.] A sample of benzene (5.0 mL, 55 mmol) was heated, in a glass-wool insulated calorimeter system, to the boiling

point. Temperature readings were recorded, to the nearest 0.1 °C, on the minute from the time of initial heating until the boiling point was attained. A heating curve (temperature °C vs. time, min) was then constructed for the pure solvent (see Figure 3). The benzene was then allowed to cool to ambient temperature, and a 5.00 mg sample of triphenylphosphine was dissolved in the benzene. The solution was then heated to the boiling point in the calorimeter system. Temperature readings were again recorded on the minute, until the boiling point of the solution was attained. The heating curve for the solution was constructed in the same fashion as that for the pure solvent (see Figure 4). The molecular weight of the solute was then determined by application of the following relationship:

$$(16) \qquad \text{M.W.} = (s/S)(K_b/\Delta T_b)(1 - k_b \Delta T_b)$$

where s is the weight of the solute, in grams, S is the weight of the solvent, in kilograms, K_b is the molal-boiling point elevation constant, and k_b is a correction constant in deg^{-1}. For benzene, K_b = 2.53 °C/m and k_b = 0.0007/°C.

The percent yield based on phosphorus tribromide (103 mg, 0.380 mmol) was determined to be 47.5%

A sample of the product in carbon disulfide solvent was submitted for FT-IR analysis. The spectrum at 4 cm^{-1} resolution is shown in Figure 5.

D. Preparation of Carbonylbis(triphenylphosphine)rhenium(II) Chloride

The synthesis of the carbonyl complex, $ReCl_2(CO)_2(PPh_3)_2$ was performed based upon a significant yield of triphenylphosphine in the preceding procedure.

Rhenium(III) chloride (880 μg, 3 μmol), triphenylphosphine (3.27 mg, 12.4 μmol), and N,N-dimethylformamide (0.370 mL, 4.80 mmol) were mixed in approximately 3-4 mL of bis-(2-methoxyethyl)ether (diglyme). The mixture was then heated in vigorous reflux at 80 °C for six hours. The resulting yellow-green solution was filtered while still hot. Warm methanol was added with stirring to the filtrate.

Upon cooling the solution was again filtered and the crystals washed with cold methanol. The filtered solution was then evaporated via a Craig recrystallization tube. The resulting residue was dissolved in 10.0 mL of a hexane/toluene mixture (1:1). The resulting solution was placed on a 50 X 1.3 cm chromatography column, made from 60-200 mesh silica gel pre-washed with hexane/toluene (1:1).

The column was initially eluted with 5.00 mL of hexane/toluene (1:1). The first 1.15 mL eluted from the column was colorless. The next 0.55 mL off the column contained a pale-yellow band. The remaining 3.30 mL, which contained a bright-green band, was evaporated to dryness. The residue was collected, washed with 2 mL of absolute ethanol, and dried in vacuo (100 °C, 0.75 mm) to yield 0.15 mg of a yellow-green complex. The percent yield (as $ReCl_2(CO)_2(PPh_3)_2$) based on rhenium(III) chloride was determined as 8.77%.

The column was next eluted with 1.50 mL of toluene followed by 0.75 mL of chloroform. The pale-yellow solution that eluted from the column was evaporated to dryness and then 2 mL of absolute ethanol was added to the residue. The pale-yellow product was collected by gravity filtration, and dried in vacuo. This complex weighed 0.16 mg and was soluble in toluene, chloroform, carbon tetrachloride, 95% w/w ethanol, and diethyl ether. The percent yield (as $ReCl_2(CO)_2(PPh_3)_2$) based upon rhenium(III) chloride as starting material was determined as 9.36%.

A sample of the pale-yellow complex in benzene was submitted for FT-IR analysis. The spectrum at 4 cm^{-1} resolution is shown in Figure 6.

The above preparation of the chlorobis(triphenylphosphine)rhenium(II) complex was repeated using refluxing 95% w/w ethanol as solvent in place of diglyme. The reaction was maintained at 80 °C for a period of six hours.

The recovered weight of the second pale-yellow fraction, from the second column elution with 0.75 mL of chloroform, following solvent evaporation and vacuum drying, was reported as 0.18 mg. Thus the percent yield (as $ReCl_2(CO)_2(PPh_3)_2$) based upon rhenium(III) chloride as precursor was reported as 10.5%.

A sample of this complex in benzene was then submitted for FT-IR analysis. This spectrum is shown in Figure 7.

A 0.1 mg sample of the complex from the second column elution from chloroform was then analyzed gravimetrically using the procedures described earlier for carbon monoxide, rhenium, triphenylphosphine, and chlorine.

Found: CO, 5.9%; Re, 25.6%; PPh_3, 60.3%; Cl, 8.0%.
Calculated: CO, 6.6%; Re, 22.2%; PPh_3, 62.5%; Cl, 8.5%.

The molecular weight of this complex, in benzene, was then determined as 570.1 g/mol by ebullioscopy.
Calculated: 574.9 g/mol

E. Preparation of Methylmagnesium Iodide

A 5 mL reaction vessel was fitted with microconnections for a distillation head, Claisen adapter, reflux condenser, thermometer, and a 1.0 mL injection syringe.

Magnesium metal turnings (1.0 g, 41 mmol) were activated by the addition of 0.3 g I_2 in 0.30 mL of dibutyl ether. Then approximately 1.5 mL of the dibutyl ether solvent was added. Next 1.0 mL of methyl iodide

(16 mmol) was added dropwise to the reaction mixture. The reaction mixture was gently warmed to initiate the reaction. An additional 0.85 mL aliquot of the solvent was added when the reaction was in progress. The methyl iodide was slowly and continuously added to the reaction mixture over a period of thirty minutes until the reaction was completed and the flask was cold.

The reaction flask was then connected to the distillation assembly which was fitted with a 5 mL receiving flask. The receiving flask contained 4.0 mL of solution saturated with potassium iodide which simultaneously was 1.1 M in silver iodide.

The Grignard solution was then cooled to approximately -78°C with a slurry of dry ice/acetone and used immediately to prepare the trimethylphosphine as described below.

F. Preparation of Trimethylphosphine

Since trimethylphosphine is a colorless, highly volatile liquid with a boiling point of 37.8 °C, it tends to undergo spontaneous combustion with atmospheric oxygen. Therefore, it must be stored under dry nitrogen as the $[P(CH_3)_3\text{-}AgI]_4$ complex. The phosphine can be regenerated later as needed. Hence this complex was prepared as follows.

Over a thirty minute interval, a 0.130 mL aliquot of phosphorus tribromide (1.3 mmol) in 250 μL of dibutyl ether was added dropwise, with continuous stirring, to the above methyl Grignard reaction mixture. Upon completion of the phosphorus tribromide addition, the reaction flask was allowed to warm to room temperature. Then using a heating mantle, the trimethylphosphine was distilled, under dry nitrogen, into a AgI-KI solution. This solution was 1.1 <u>M</u> AgI saturated with KI. When the still-pot temperature attained 100 °C, an excess of saturated ammonium chloride solution was added, dropwise, to the reaction mixture to ensure complete hydrolysis of the $P(CH_3)_3$-Grignard complex. The $[P(CH_3)_3\text{-AgI}]_4$ complex was collected by gravity filtration, washed first with saturated potassium iodide solution, then washed with water, and finally dried over anhydrous magnesium sulfate.

The $[P(CH_3)_3\text{-AgI}]_4$ complex weighed 2.26 g. The percent yield of trimethylphosphine, based on phosphorus tribromide, is reported as 34.9%.

A sample of the trimethylphosphine in carbon disulfide was submitted for FT-IR spectral analysis. The spectrum, with carbon disulfide acting as reference, is shown in Figure 8.

The molecular weight of the trimethylphosphine in diethyl ether was determined by the ebullioscopic procedure described above to be 73.5 g/mol.
Calculated: 75.9 g/mol

G. Preparation of Carbonyltetrakis(trimethylphosphine)rhenium(I) Chloride

The previously prepared trimethylphosphine was regenerated from the silver iodide complex by heating in vacuo for one hour at 100 °C and 0.75 mm. The trimethylphosphine vapors were condensed using a dry ice/acetone slush bath.

A 2.2 mg aliquot of the freshly prepared trimethylphosphine (28.9 μmol) was condensed into the reaction vessel containing 0.16 mg of carbonylbis(triphenylphosphine)rhenium(II) chloride (281 nmol) suspended in 5.0 mL of benzene. The reaction mixture was then heated at reflux temperature (80 °C) for one hour. The resulting suspension was filtered in air, and the solid washed with benzene. The complex was recrystallized from a mixture of benzene/methanol (1:1). The yield was determined to be 0.130 mg, based on carbonylbis(triphenylphosphine)rhenium(II) chloride.

The percent yield of the complex (as $ReCl(CO)(PMe_3)_4$), based on $ReCl_2(CO)_2(PPh_3)_2$, is 84.4%.

The molecular weight of the complex in methylene chloride was determined by the ebullioscopic procedure described above to be 549 g/mol.

Calculated: 553 g/mol

1. Single Crystal Preparation

A mixture of tetrahydrofuran and diethyl ether

(1:1) was added to an acetonitrile solution of the compound, followed by the slow addition of diethyl ether. The resulting slurry was filtered to recover the solid product and the product recrystallized from benzene/ methanol (1:1).

In an attempt to improve the yield of the product, the above synthesis was repeated except 95% w/w ethanol was employed as the solvent in place of benzene. The product was then recrystallized from benzene/methanol (1:1) with a yield, again based on $ReCl_2(CO)_2(PPh_3)_2$, of 0.135 mg.

Again, single crystals of the complex were prepared by the previously described procedure, and a 0.100 mg sample was analyzed gravimetrically by the procedure mentioned above.

Calculated: CO, 5%; PMe_3, 55%; Cl, 6%; Re, 34%.

Found: CO, 4.5%; PMe_3, 60.0%; Cl, 5.9%; Re, 29.6%.

Following the preparation of additional $ReCl_2(CO)_2(PPh_3)_2$, the above procedure was once again repeated in an attempt to possibly further improve the overall percent recovery of the complex $ReCl(CO)(PMe_3)_4$. The synthetic route beginning from $ReCl_2(CO)_2(PPh_3)_2$ was repeated. This time benzene/ethanol (1:1) was used as the solvent in place of 95%(w/w)ethanol. The reaction time was increased to 3 hrs. at 80 °C reflux. The resulting yellow-brown solution was filtered in air, washed with benzene/ethanol (1:1), and then recrystallized from benzene/ethanol (1:1). The resulting crystals were dried in vacuo 0.75 mm at 100 °C, for 12 hrs. The lemon-yellow crystals were recrystallized from an ice-cold mixture of methylene chloride/ethanol (1:1). The product yield (as $ReCl(CO)(PMe_3)_4$) was 0.134 mg, 93.1%, based upon 0.15 mg of $ReCl_2(CO)_2(PPh_3)_2$ as starting material. An additional preparation of $ReCl_2(CO)_2(PPh_3)_2$ yielded 0.170 mg of product.

To investigate if the product purity would be further enhanced by utilizing either 2-diethylaminoethanol or triethanolamine as the solvent instead of a mixture of benzene/ethanol (1:1), the original synthesis was once again initiated with 0.150 mg of $ReCl_2(CO)_2(PPh_3)_2$ (260 n mol) and 2.2 mg of trimethylphosphine (28.9 μmol) suspended in 5.0 mL of triethanolamine. The reaction was maintained at reflux temperature (80 °C) for a period of six to seven hours. At the end of this period, the pale-yellow solution was filtered in air, and the crystals washed with benzene/ethanol (1:1). The lemon-yellow crystals were twice recrystallized from ice-cold methylene chloride/ethanol (1:1), followed by vacuum drying (100 °C, 0.75 mm) for 24 hrs. The product yield (as $ReCl(CO)(PMe_3)_4$) of 0.137 mg of the yellow-white crystals was 95.1%, based on $ReCl_2(CO)_2(PPh_3)_2$.

Single crystals of the product were prepared by the method described previously, and a 0.100 mg sample was analyzed gravimetrically for carbon monoxide, trimethylphosphine, chlorine, and rhenium.

Found: CO, 4.7%; PMe_3, 60.3%; Cl, 6.0%; Re, 29.0%.

Calculated: CO, 5.0%; PMe_3, 55.0%; Cl, 7.0%; Re, 34.0%.

A sample of the crystals in benzene was then submitted for FT-IR analysis. The spectrum is presented in Figure 9.

The complex is a yellow-white solid that is soluble in non-polar solvents but insoluble in polar solvents such as ethanol and water. The solid is stable in air for fairly long periods. Very slow decomposition, probably caused by reaction with atmospheric water, is observed over several days. Solutions of the complex are pale-yellow, have an odor of free trimethylphosphine, and show a strong IR peak at 1780 cm^{-1}.

The molecular weight of the complex was determined in methylene chloride by the ebullioscopic procedure as described above to be 549.2 g/mol.

Calculated: 553.2 g/mol

III. DISCUSSION

A. Preparation of Triphenylphosphine

A convenient microscale preparation of triphenylphosphine was effectively performed. This involved a Grignard reaction of bromobenzene and phosphorus tribromide with magnesium in anhydrous diethyl ether. The reaction required a total of two hours forty-five minutes at reflux temperature: 45 minutes for the preparation of the phenylmagnesium bromide Grignard reagent and two hours for the preparation of the triphenylphosphine.

Following alkaline hydrolysis with dilute sodium hydroxide solution, two recrystallizations from a mixture of isopropanol and petroleum ether, one recrystallization from absolute ethanol, and sublimation in vacuo (80 °C, 0.75 mm), pure, white, needle-like crystals formed in 47.5% yield. These white crystals were established as those of triphenylphosphine as they exhibited melting behavior in the range 75.0 °C-79.0 °C. Pure triphenylphosphine is characterized by a melting point range of 79.0 °C- 80.0 °C. The molecular weight of these crystals in pure benzene solvent was ascertained by an ebullioscopic procedure as being 259.3 g/mol. The calculated molecular weight of triphenylphosphine is 262.0 g/mol.

A sample of the crystals in carbon disulfide solvent gave vibrational bands in the infrared as reported in Table II.

The solvent for the FT-IR spectrophotometric analysis was selected so as to minimize the interference of band overlapping. Vibrational assignments of absorption bands are necessary for the interpretation of spectral data. Thus, bands commonly found in the 3000 cm^{-1} region are characteristic of C-H stretching. Characteristic bands near 1650 cm^{-1} and 1525 cm^{-1} appear in the spectra of all of the compounds containing a phenyl group. Bands in the region 1475 cm^{-1} to 1375 cm^{-1} arise mainly from C-H deformation vibrations. The P-C band sometimes appears as a doublet. In triphenylphosphine, this band appears at 1180 cm^{-1}. The position of this band is dependent upon the electronegativity of the other groups attached to the phosphorus atom; the lower the electronegativity, the longer the wavelength of the band.

The P-C bonds in the phosphine compounds associated with aromatic groups give rise to a weak band at 1000 cm^{-1} and a strong band at longer wavelengths. Typically, C-C vibrations absorb in the 1100 cm^{-1} region and Si-C vibrations near 800 cm^{-1}; thus the strong P-C vibration would be expected to be found below 800 cm^{-1}. Due to the high electronegativity of the phosphorus atom, the band would be expected in the region below 700 cm^{-1} for triphenylphosphine.

The vibrational frequencies of functional groups appear to be rather constant with varying environmental conditions; however they tend to be influenced by electrical fields in the vicinity of oscillating molecular species. This is particularly evident as the physical state of the molecule changes. Molecular interaction results from electrostatic attractive forces existing between sets of oscillating dipoles. Hydrogen bonding can induce band shifts of functional groups and other regions due to the change in the charge distribution of the molecule.

The vibrational spectral data for the previously prepared product in CS_2 solvent tend to coincide rather well with the spectral data for triphenylphosphine, in CS_2 solvent (see Table II). The observed molecular interaction effects appear to be self-consistent. The prominent effects appear to be associated with:
1) hydrogen bonding between phosphoryl and hydrogen groups and 2) dipolar interaction between phenyl groups and P-C bonds.

A detailed study of the infrared vibrational assignments of the previously prepared triphenylphosphine could be undertaken, at a later date, in an attempt to investigate the band relationships with varying environmental conditions. Some suggested media for analysis would include isopropyl alcohol, methyl acetate, cellulose monoacetate film, and mineral oil.

One would expect the vibrational frequencies of the functional groups of the molecule to remain fairly constant under different conditions; however, the interaction effects that do occur are modified by the influence of electronic oscillating molecules.

B. Preparation of Carbonylbis(triphenylphosphine)-rhenium(II) Chloride

The recovery of triphenylphosphine from the previous synthesis in sufficient yield and purity warranted an attempt to prepare the species $ReCl_2(CO)_2(PPh_3)_2$.

It appears as though the reaction of rhenium(III) tertiary phosphine complexes in N,N-dimethylformamide (DMF) undergo reaction with the solvent (see Figure 10).

The carbonyl group is introduced into these complexes via reaction of DMF in refluxing diglyme, ethanol, methanol, or 2-methoxyethanol. The overall percent yield of these compounds is affected by the choice of solvent with the yield increasing in the order: diglyme $<$ ethanol $<$ methanol $<$ 2-methoxyethanol. This reaction quite possibly also might occur in non-alcoholic, oxygen-containing solvents such as tetrahydrofuran [51]. Thus, it is possible that the carbonylation properties of these compounds follow a mechanistic pathway similar to aldehydes and ketones.

For those compounds studied, the carbonyl group change occurs via a five-coordinate CO adduct in which e two carbonyls are equivalent. This CO exchange in $Cl_2(CO)_2(PPh_3)_2$ would require an intermediate complex which the entering and leaving CO molecules are indisnguishable.

The carbonylation reactions in this study tended o produce a mixture of products which was thought to onsist of the following species: $ReCl(CO)_3(PPh_3)_2$, $e_2Cl_5(PPh_3)_3$, $Re_2Cl_6(PPh_3)_2$, and trans-$ReCl_4(PPh_3)_2$. The product distribution was influenced by the choice of solvent and the reaction time.

Reactions in refluxing ethanol for periods of six hours afforded the best yield of $ReCl_2(CO)_2(PPh_3)_2$. However, some of the grass-green dimeric product, $Re_2Cl_2(PPh_3)_2$, also was formed.

Separation of this mixture by conventional column chromatography, on silica gel was necessary. Thus following three column elutions with hexane/toluene (1:1) as the mobile phase, and recrystallization of the forest-green crystals from ice-cold methanol, well formed yellow-green crystals of a complex that was thought to be $ReCl_2(CO)_2(PPh_3)_2$ were produced. However, upon drying a portion of the product in vacuo (100 °C, 0.75 mm), the crystals turned to powder. One possibility is that the yellow-green crystalline product was the oxygen adduct $[ReCl_2(CO)_2(PPh_3)_2]O_2$ and that drying generated the $ReCl_2(CO)_2(PPh_3)_2$, an amorphous powder.

The FT-IR spectrum of the powder form in benzene produced a very strong carbonyl absorption at 1906 cm^{-1}. The Re-Cl vibrational band was thought to be at a much lower frequency, which is below the "window" characterized by KBr optics. However, the Re-Cl band might be observed if CsCl optics were used to scan the region 3300 cm^{-1} - 300 cm^{-1}.

The molecular weight of the complex in benzene was determined as 570 g/mol. The calculated weight of $ReCl_2(CO)_2(PPh_3)_2$ is 574 g/mol.

Gravimetric analysis of a 0.1 mg sample of the complex afforded 0.0700 mg (60.3%) of triphenylphosphine and 0.00753 mg (5.9%) of carbon monoxide. These experimentally determined quantities appear to coincide rather well with a complex possessing a $ReCl_2(CO)_2(PPh_3)_2$ formula.

The $ReCl_2(CO)_2(PPh_3)_2$ complex was soluble in a variety of non-polar solvents and the FT-IR spectrum appears to be in accord with the trans-disposition of both Re-CO and Re-Cl bonds, possessing both single ν(CO) and ν(Re-Cl) absorptions (see Table I). Thus, it most likely exhibits an all-trans geometry. This type of structural arrangement would be in accord with a less sterically strained structure than that which would result if the bulky triphenylphosphine groups were in a cis-configuration (see Figure 11).

The characterization of the cis and trans dispositions of the complex can be accomplished, rather nicely, by a convenient modification of the Cotton-Kraihanzel [1] model for the interpretation of vibrational spectra and bonding in phosphine-substituted metal carbonyls. Basically, this model analyzes and assigns the infrared-active carbonyl stretching frequencies of simple and substituted metal carbonyls of the type $ML_x(CO)_{6-x}$. These complexes possess an essentially octahedral distribution of the ligands and carbonyl groups about the metal atom. The model involves qualitative and semi-quantitative inferences from valence theory to assign the signs and relative magnitudes of CO stretching force constants and the coefficients of quadratic interaction terms coupling the stretching motions of different carbonyl groups. The frequencies of the normal modes of vibration can only be correlated with the electronic structure if the observed bands are correctly assigned. Thus, there are three important criteria for making such assignments. First, the relative intensities of the infrared bands provides clues to their assignments to the normal modes. Secondly, the measurement of the polarization of Raman lines can give positive evidence for assignments of some bands. Third, deductions from valence theory about the relative magnitudes of force constants yield additional information to select correct assignments.

The relative magnitudes and signs of stretch-stretch interaction constants can sometimes be obtained from valence bond theory. In a metal carbonyl having six octahedrally disposed ligands, the valence shell orbitals of the metal fall into three groups (see Table III). If the p-orbitals are used in σ-bonding, in order that a full set of six octahedral hybrid orbitals spanning the representations $A_{1g} + E_{1g} + T_{1u}$ are formed, then only the T_{2g} orbitals remain for π-bonding. For symmetry reasons, these orbitals cannot mix with others of the valence shell so that to a first-order approximation the metal-ligand π-bonding is treated separately from the σ-bonding.

Thus, "factoring out" the pi bonding using this type of symmetry relation and considering in detail the directional properties of metal d-π orbitals, the following deductions can be made as a method for elucidating the electronic structure of cis and trans species. Following Jones [52] these deductions can be stated as follows:

1) All (CO stretching)-(CO stretching) interactions should give rise to terms in the potential energy expression with positive coefficients (interaction force constants).

2) If k_c and k_t are the interaction constants between pairs of cis and trans CO groups, respectively, then it is expected that $k_t = 2k_c$.

3) The CO stretching force constants should decrease steadily as CO groups are successively replaced

by other ligands which are less demanding for metal d-π electrons.

4) The CO groups cis to substituents of this type such as the phosphine should have higher stretching force constants than those trans to substituents.

5) Stretch-stretch interaction constants should probably increase with increasing replacement of CO by ligands of lower pi bonding ability.

A detailed analysis of the symmetry properties of the complex coupled with the determination of the interaction force constants should effectively characterize the prepared species $ReCl_2(CO)_2(PPh_3)_2$ as having either cis or trans geometry.

In this approximation coupling between CO groups is assumed to be entirely non-mechanical. This is a valid approximation in view of the fact that any pair of carbonyls is separated by two intervening weak bonds and a metal atom. Thus, mathematically, this involves the solution of an inverse $G(G^{-1})$ matrix. This matrix is the unit matrix of appropriate dimension multiplied by the reciprocal of the reduced mass of the CO oscillator.

The F matrices are used to express the matrix elements as algebraic sums of CO stretching constants, k_1, k_2, and one or more stretch-stretch interaction constants, k_c, k_c', representing interaction of cis pairs of

CO groups and k_t, representing interaction of a trans pair of CO groups.

[Note: The G matrix is used to relate the kinetic energy of a vibrational mode to the internal and symmetry coordinates:

$$(17) \quad G = \sum_{k=1}^{3N} \mu_k B_{ik} B_{jk} \quad (i,j = 1,2,3,...3N-6)$$

where μ_k is the reciprocal of the reduced mass of the CO oscillator, and B represents elements of the matrix transforming the Cartesian coordinates to the internal coordinates with k denoting the atom and i,j denoting coordinates.

The F matrix contains the diagonal elements of the potential energy terms which are necessary for a solution of a particular problem.

$$(18) \quad V = \tfrac{1}{2}\mathbf{RFR}$$

where **R** is a column vector whose components are the 3N-6 internal coordinates and **F** is a (3N-6) X (3N-6) matrix whose terms are the coefficients in the potential energy expression.]

There are several known types of octahedral carbonyls and substituted carbonyls: $M(CO)_6$, $ML(CO)_5$, cis-$ML_2(CO)_4$, trans-$ML_2(CO)_4$, cis-$ML_3(CO)_3$, trans-$ML_3(CO)_3$ cis-$ML_4(CO)_2$, and trans-$ML_4(CO)_2$. The "approximate" secular equations in which the following substitutions $k_i = k_c = k_c' = k_t/2$ have been applied, symmetry properties, and infrared activity fundamentals for these octahedral species are shown in Table IV.

Comparison of the infrared absorption bands for the complex $ReCl_2(CO)_2(PPh_3)_2$ in benzene solvent given in Table V with the equations in Table IV indicates that the relative energies of the bands are consistent with the conclusion from valence theory that the stretch-stretch interaction constant must be positive. The force constants of the complex were then determined using the "approximate" equations in Table IV.

In the phosphine substituted complexes, a reasonable approximation to begin with is that the metal-phosphorus bonds are axially symmetric. The symmetries and selection rules given in Table IV are applicable only when such an assumption is made.

For the complex $ReCl_2(CO)_2(PPh_3)_2$, a discussion of the assignments used in calculating the force constants follows.

From the data in Table V, the cis-$ML_4(CO)_2$ complexes possess C_{2v} symmetry and an infrared active A_1 fundamental while the trans-species possess D_{4h} symmetry and an infrared active A_{2u} fundamental. For these complexes the assignments tend to follow unambiguously from the secular equations and the one reported band may be assigned unequivocally from the selection rules. Therefore, when this assignment is used to evaluate the force constants k_i and k_t, the results shown in Table VI are obtained.

However, the resulting force constants must clearly reflect that the five rules, proposed previously, are consistent with all of the experimental data in order to ensure the validity of the assignment. If the assignment is not consistent with each of the five rules, then it is unacceptable since it cannot be used to give real and characterizable force constants. Using rules 1 and 2, the force constants that were obtained appear to be in accord with the expectations of rules 3-5.

If an incorrect assignment is made, based upon the secular equations for a complex of a given symmetry type, then imaginary roots will be obtained for the force constants. As can be seen in Table VI, the vibrational band assignment of 1906 cm^{-1} was in accordance with the five rules and produced real force constants from the secular equations of symmetry, D_{4h}. When the secular equations of symmetry C_{2v} were used to determine the force constants, the same vibrational assignment gave a negative value for k_i and imaginary roots. Based upon this evidence, the complex apparently possesses an all trans geometry.

The carbonyl group exchange most likely occurs via a five coordinate CO adduct in which the two carbonyls are equivalent. This CO exchange in $ReCl_2(CO)_2(PPh_3)_2$ requires an intermediate complex in which the entering and leaving CO molecules are indistinguishable.

Thus, of the possible geometric isomers of $ReCl_2(CO)_2(PPh_3)_2$, the trans disposition allows the two CO ligands to occupy equivalent positions and represents a minimum modification of the parent structure. Due to the reversibility of the carbonylation reactions, the triphenylphosphine ligands also retain their trans dispositions.

An extension of this investigation would be a single crystal X-ray structure to precisely determine the structure of the complex $ReCl_2(CO)_2(PPh_3)_2$. This would also verify the trans disposition of the CO ligands. Positional parameters, bond angles, and bond distances could be determined and an ORTEP model of the molecule constructed. From this type of arrangement, then, the octahedral structure and the trans dispositions of all of the ligands should be obvious.

One further note concerning the solution chemistry of this type of carbonylation reaction is that the reactions between DMF and $ReCl_2(CO)_2(PPh_3)_2$ in refluxing diglyme or 95% w/w ethanol are known to be complex and lead to the formation of mixtures. The possible product distributions can be summarized by examination of Figure 12. The Re-Re bond cleavage reaction that takes place in solution appears to be complicated by a variety of competing redox reactions. These factors cause $Re_2Cl_2(PPh_3)_2$

and $ReCl_2(CO)_2(PPh_3)_2$ to be converted to $ReCl(CO)_3(PPh_3)_2$, $Re_2Cl_5(PPh_3)_2$, $Re_2Cl_6(PPh_3)_2$, and $ReCl_4(PPh_3)_2$. The product distribution of these various redox reactions in solution can be succinctly summarized in Figure 13. This redox phenomenon possibly could account for the low product yield of the complex $ReCl_2(CO)_2(PPh_3)_2$. The yield does not appear to be increased with the addition of triphenylphosphine, or dimethylformamide, or both reagents to the reaction solution.

C. Preparation of Trimethylphosphine

Preliminary efforts to prepare trimethylphosphine were unsuccessful. The primary reason that the trimethylphosphine was not formed probably was due to the fact that the Grignard reaction mixture was too hot. Since the synthesis of trialkylphosphines would appear to be very successful at reaction mixture temperatures of -50 °C or below, the microscale preparation of trimethylphosphine was repeated. This time the temperature of the Grignard reaction mixture was decreased to -78 °C via a dry ice/acetone slush bath. The preparation of the trimethylphosphine was then repeated as described in the above procedure.

The preparation of trimethylphosphine utilizing an organomagnesium intermediate in dibutyl ether was effected in a rather good yield of 34.9%. The low reaction temperature was found to be critical to the formaon of the compound. Actually, the lower the Grignard action temperature, the better the product yield.

Somewhat improved yields of tertiary phosphines, rimethylphosphine in particular, have been produced tilizing organo lead and organo zinc reagents [16]. omplete alkylation of phosphorus halogen compounds is atalyzed by aluminum trichloride and higher temperatures ($\sim$100 °C). The major disadvantage of this particular ethod is that the reaction conditions need to be more precisely controlled owing to the extremely high reactivity of the organo lead and organo zinc reagents. In fact, the synthesis should be performed using a high vacuum system.

The observed infrared vibrational bands appear to attest to the purity of the final product. Vibrational bands occuring near 3000 cm^{-1} are characteristic of C-H stretching. The C-H deformation vibrations commonly can be seen in the 1350 cm^{-1} - 1450 cm^{-1} region. The antisymmetric vibration of the PC$_3$ pyramid appears in the region 710 cm^{-1} - 900 cm^{-1}. The P-C bond vibrations tend to occur at longer wavelengths in trialkylphosphines than they do in triarylphosphines. That this is the case can be seen by comparing Figures 5 and 8. The C-C vibrations appear to absorb in the region 1000 cm^{-1} - 1100 cm^{-1}.

The molecular weight of trimethylphosphine in diethyl ether was determined by an ebullioscopic procedure to be 74 g/mol as compared to a calculated value of 76 g/mol.

This molecular weight information coupled with the infrared spectroscopic data confirmed that the desired product was produced in sufficient purity so as to warrant a microscale preparation of the complex $ReCl(CO)(PMe_3)_4$.

D. Preparation of Carbonyltetrakis(trimethylphosphine)rhenium(I) Chloride

The recent developments in the chemistry of the heavier transition metals are, to a large extent, a result of the widespread use of derivatives such as tertiary organic phosphine and arsine complexes, which are soluble in organic solvents. The properties of mononuclear complexes of tertiary phosphines and arsines with metal halides have been established in some detail for Pt(II), Pt(IV), Pd(II), Ir(III), and Rh(III). However, little is known of those of osmium, ruthenium, and rhenium [53].

The chemistry of rhenium is developing rapidly. The chlorocarbonyl complex of type $ReX(CO)(L)_4$, where X= Cl and L is a monodentate ligand (here as trimethylphosphine), was prepared during these investigations.

The reaction of trimethylphosphine with the complex $ReCl_2(CO)_2(PPh_3)_2$ was carried out several times in a variety of refluxing organic solvents. The organic solvents that were employed for this reaction were ben

ne, benzene/ethanol (1:1), 95% w/w ethanol, and tri-
thanolamine, respectively. For each solvent, the re-
tion produced the species $ReCl(CO)(PMe_3)_4$ as the
rincipal product. The complex appears to be octahedral
nd monomeric with each of these reaction conditions.
he product yield appears to increase in the solvent
rder: triethanolamine > 95% w/w ethanol > benzene/
thanol (1:1) > benzene. The values of the C-O stretching
odes obtained from the infrared spectrum of the complex
indicate the π -character of the metal ligand bonds.
The formation of the species $ReCl(CO)(PMe_3)_4$ (as a result of the reaction of trimethylphosphine with the complex $ReCl_2(CO)_2(PPh_3)_2$ in benzene) gives an 84.4% yield. This complex is suspected of being oxidized by two equivalents of molecular chlorine to $ReCl_3(CO)(PMe_3)_3$. Further investigation by treatment of $ReCl(CO)(PMe_3)_4$ with chlorine in carbon tetrachloride should confirm this phenomenon. The yield of the complex $ReCl(CO)(PMe_3)_4$ is not expected to increase if additional trimethylphosphine is added to the reaction solution because the reaction outcome is more dependent upon the choice of solvent and the reaction time rather than the quantity of the reacting species. The preferred configuration of the final product is shown in Figure 14.

The reaction time appeared to have a significant effect on the composition and purity of the final product as well as the type of refluxing solvent. Thus, for reaction times of one to two hours in refluxing benzene, two or more complexes appear to have been formed. The possible products of this particular reaction, in addition to the major product $ReCl(CO)(PMe_3)_4$, could be $ReCl(CO)_2(PMe_3)_3$ and $ReCl_2(CO)_2(PMe_3)_2$. The final product distribution could be resolved by proton NMR.

Recrystallization of the product from a benzene/methanol (1:1) solution produced rather well-defined octahedral, lemon-yellow crystals.

In order to determine if an increase in the purity of the major product and an increase in overall yield could be obtained, the preparation of the complex was performed in 95% w/w ethanol as the refluxing solvent in place of benzene. The yield was slightly increased from 0.130 mg to 0.135 mg. This indicates that the choice of solvent media definitely has an effect on the outcome of the reaction and the production of the final products. Gravimetric analysis results also indicate that the complex $ReCl(CO)(PMe_3)_4$ was obtained in sufficient purity. The results of this analysis also tend to indicate that four trimethylphosphine ligands are associated with one carbonyl moeity in the complex. Following the recrystallization from a mixture of benzene/methanol (1:1), yellow crystals of the complex were recovered. The yellow color of the crystals was slightly fainter than the lemon-color of the previous crop. Again, the crystals appeared to be octahedrally shaped as did the previous crop.

When the preparation of the complex $ReCl(CO)(PMe_3)_4$ was carried out in a mixture of benzene/methanol (1:1), from 0.14 mg of $ReCl_2(CO)_2(PPh_3)_2$ as precursor, the yield of the recovered product decreased somewhat from 0.135 mg to 0.134 mg. Following recrystallization of the product from ice-cold methylene chloride/ethanol (1:1), the percent yield based on the precursor $ReCl_2(CO)_2(PPh_3)_2$ was 93.7%. These results would tend to indicate that a solvent mixture for the reaction medium is not as effective as that of a pure or nearly pure solvent.

Further investigations involving the selection of a solvent medium such as 2-diethylaminoethanol or triethanolamine were undertaken in order to obtain the major product in greater purity and yield.

As a result of previous experience involving the preparation of the precursor $ReCl_2(CO)_2(PPh_3)_2$, the reaction period was increased to seven hours at 80 °C reflux. This was done to improve the yield of the desired complex.

In fact, after two recrystallizations from an ice-cold mixture of methylene chloride/ethanol (1:1) and vacuum drying, the resulting pale-yellow crystals were obtained in 95.1% yield. Thus, the selection of triethanolamine as the solvent medium appeared to significantly improve the overall yield of the desired product. The existing reaction conditions, the experimental apparatus, and the inherent nature of the reactants appear to be limiting factors on the overall yield of the product.

The results of the gravimetric analysis with several crystals of the complex suggest a configuration of the complex which is in accord with Figure 14. Thus, one can conclude that four trimethylphosphine substituents are associated with one carbonyl moeity in the complex.

Solution FT-IR spectra were selected in preference to Nujol^R mull spectra. Chloroform was found suitable as far as solubility and decomposition of ReCl(CO)-(PMe$_3$)$_4$ were concerned. The primary purpose of the spectroscopic analysis was to obtain the frequencies of the bands due to the ReCl(CO) group. A complete vibrational assignment of either P(CH$_3$)$_3$ or the PPh$_3$ ligand was not attempted.

The measured frequencies and the characteristics of the infrared absorption bands are reported in Table VII. The spectrum was scanned from 5000 cm^{-1} to 1000 cm^{-1}.

The bands in the region 2800 cm^{-1} - 2900 cm^{-1} are characteristic of C-H stretching. The characteristic bands near 1000 cm^{-1} seem to be connected with the frequency of the antisymmetric vibration of the PC$_3$ pyramid. The trimethylphosphine substituents absorb in this region. Bands in the region 1400 cm^{-1} - 1300 cm^{-1} arise mainly from C-H deformation vibrations. The

C-C vibrations absorb in the 1100 cm^{-1} - 1200 cm^{-1} region. The spectrum shows an intense carbonyl absorption at 1780 cm^{-1}. As was assumed in the spectrum of the complex, $ReCl_2(CO)_2(PPh_3)_2$, the Re-Cl stretching vibrations probably absorb in the 290 cm^{-1} - 310 cm^{-1} region. This particular region is below the optical "window" exhibited by KBr optics. As was mentioned previously, the width of this optical "window" could be enhanced if the spectrophotometer were equipped with a CsBr or CsCl optical bench.

Comparison of the infrared spectrum of $ReCl_2(CO)_2$-$(PPh_3)_2$ with that of $ReCl(CO)(PMe_3)_4$ (see Figure 7 and 9) suggests that the more basic the ligands the lower the CO stretching frequency. Also, in accord with the Cotton-Kraihanzel force constant method, as the number of CO moeities are successively replaced by phosphine substituents, the CO stretching frequencies decrease.

The pale-yellow crystals are moderately soluble in polar solvents and are stable under dry nitrogen for several months. Slow decomposition of the crystals in moist air results in extreme darkening to a brown color over a period of several days. The solutions, however, appear to be quite sensitive to moist air and oxidize readily with the release of trimethylphosphine. The solutions undergo a color change from pale-yellow to dark-yellow.

The results of the gravimetric analysis and of the infrared vibrational assignments suggest that the structure of the complex resembles that of a regular octahedron with the phosphine groups in approximately equatorial positions and the carbonyl and chlorine in approximately axial positions. This can be seen with reference to Figure 14.

IV. DISCUSSION FOR ADDITIONAL INVESTIGATION

A. Homogeneous Catalysis with Rhenium Carbonyl Complexes

The complex hydride chlorotetrakis(trimethylphosphine)rhodium(I), $RhClH(PMe_3)_4$, has been shown to be an effective catalyst for the homogeneous hydrogenation of a variety of unsaturated substances [54]. Since a close formal analogy appears to exist between this rhodium complex and the rhenium complex, hydridochlorotetrakis-(trimethylphosphine)rhenium(II), $ReClH(PMe_3)_4$ (eg. both dissociate in benzene/ethanol solutions to give coordinatively unsaturated species), it seems likely that the rhenium complex also would act as a catalyst. Further investigation would suggest that the hydrido rhenium complex can be prepared by interaction of the chloro carbonyl, $ReCl(CO)(PMe_3)_4$, with molecular hydrogen at ambient temperature and pressure in the presence of a base such as triethanolamine.

Since hydrido complexes have a tendency to be very reactive chemically, reactions of the complex with a variety of unsaturated substances could be performed and the products monitored to determine if hydrogenation at the site(s) of unsaturation had, in fact, occured [55].

The chemical reactions that would most likely form well-defined, characterizable products are as follows: 1) treatment of a benzene/ethanol solution of $ReHCl(PMe_3)_4$ with 2,2-bipyridyl in excess under nitrogen, 2) treatment of a benzene/ethanol solution of $ReHCl(PMe_3)_4$ with an excess of norbornadiene, 3) treatment of benzene/ethanol solutions of $ReHCl(PMe_3)_4$ with hex-1-yne, oct-1-yne, or phenylacetylene, 4) treatment of benzene/ethanol solutions with penta-1,3-diene, cis and trans-hexa-1,4-diene, 2-methyl-hexa-1,5-diene, or cyclo-octa-1,5-diene should produce saturated products, and 5) treatment of a saturated solution of the hydride in chloroform frozen in a thick-walled tube with ethylene condensed in followed by gradual warming of the tube should produce saturated products [56].

B. "Mixed" Derivatives of Rhenium Carbonyl Complexes

The present work merely focused on the preparation of single derivatives of rhenium carbonyl species, that is those complexes containing only one type of non-carbonyl substituent group. However, further investigation would prompt a microscale preparation of "mixed" derivatives of complexes of the type $ReCl_2(CO)_2XY$ where X = 2,2-dipyridyl and Y = various monodentate Lewis bases. Most likely the Y ligands would occupy trans positions. The Y ligands could conceivably consist of the following bases: 1) pyridine, 2) ammonia, 3) triphenylphosphine, 4) trimethylphosphine, and 5) several phosphites [57,58].

These complexes are of particular interest in that the CO stretching spectra are readily interpretable through consideration of the differing bonding properties of the substituent groups. Thus, an internal comparison of bonding properties for two different ligands would be possible. Further application of the secular equations of Cotton and Kraihanzel to the determination of CO stretching and CO-CO interaction force constants for complexes of the type $ReCl_2(CO)_2XY$ yield real roots. This determination would tend to indicate that the secular equations can distinguish between two physically different cis-CO-CO interaction constants. These two k_i, involving the coupling of two carbonyls each trans to a nitrogen and the second trans to a phosphorus, may differ appreciably as differences in the bonding properties of 2,2-dipyridyl and the phosphine become more pronounced. (The π-accepting ability of the phosphorus-containing ligand is greater than that of the amines.) Further, one would expect that $k_{i(xy)} < k_{i(xx)}$ since the more strongly π-accepting phosphorus atom is better able to compete with the carbonyls for metallic d-π electrons, thus diminishing the interaction effect. As has often been the case, the number of parameters within the Cotton-Kraihanzel secular equations is limited by the number of experimental carbonyl stretching frequencies available. One would surmise that for this reason the approximation $k_{i(xy)} = k_{i(xx)}$ was explicitly adopted in the first place.

these parameters decrease in the expected order as the qualitative order of π-accepting ability of the phosphorus-containing ligand increases. Real force constants can thus be obtained by adjusting $k_{i(xy)}/k_{i(xx)}$ in a physically reasonable way for Y ligands of varying bonding ability.

Since metal-ligand "back bonding" is weaker in the rhenium complexes, carbonyl stretching frequencies for the rhenium complexes should be somewhat higher than for the corresponding Group VI B derivatives. This also would minimize differences in the cis interaction constants.

Thus, for octahedral derivatives of the type $ReCl_2(CO)_2XY$, the X and Y ligands should occupy sites trans to the carbonyls. This phenomenon is proposed on the basis of the directive influences of substituent groups. If this is the case, only one type of cis CO-CO interaction is possible because the structure is uniquely defined. Again CO stretching frequencies and force constants should be consistent with commonly held assessments of the bonding properties of various Y ligands. The higher energy band of the two expected CO stretching vibrations ($A_1 + B_1$, C_{2v} local symmetry) can be assigned as the more symmetrical A_1 mode.

Since mixing of σ and π bonding can occur in octahedral metal carbonyl derivatives, σ-bonding properties of ligands can exert an influence on the CO stretchng frequencies in such complexes. Thus, the lower the lectronegativity and the greater the basicity of the ubstituent ligand, the lower the CO stretching frequency.

V. SUMMARY

The results of the current work indicate that rhenium carbonyl complexes of the type $ReCl_2(CO)_2(PPh_3)_2$ can be prepared in moderate yield by implementation of a microscale organic synthesis. The reaction is initiated from the precursors triphenylphosphine, rhenium(III) chloride, and N,N-dimethylformamide in refluxing ethanol solvent. The overall nature of the reacting species tends to limit resulting product yields. Since the reaction produces isomeric mixtures of products, the desired product(s) must be resolved by conventional column chromatography. The desired product outcome tends to be strongly influenced by reaction times and solvent solubility.

The possible geometric isomers of the complex $ReCl_2(CO)_2(PPh_3)_2$ are the cis and trans dispositions (see Figure 15). The trans disposition appears to be in accordance with FT-IR spectral data and force constant calculations. The FT-IR spectrum indicates a single carbonyl stretching frequency at 1906 cm^{-1}, indicating that the CO groups are in an equivalent configuration around the central metal which most likely represents an all-trans geometry of the complex.

The complex appears to be stable for periods of several months in an atmosphere of oxygen-free nitrogen.

The complex, over the course of several days, slowly decomposes in air.

The preparation of the complex $ReCl(CO)(PMe_3)_4$ was also successful on the microscale. Pale-yellow crystals of the complex were recovered from methylene chloride/ethanol solutions in significant yield.

The largest product yields resulted from refluxing a mixture of the precursors, trimethylphosphine and $ReCl_2(CO)_2(PPh_3)_2$, together in viscous solvent media such as triethanolamine. Also, pure solvents were more effective toward producing the target species than were mixed solvents.

Trimethylphosphine replaces the triphenylphosphine ligands in the complex $ReCl_2(CO)_2(PPh_3)_2$, primarily due to the differences in the basicities of the substituent groups. The FT-IR spectrum indicates a single CO stretching frequency near 1780 cm^{-1}. This lower frequency is thought to be attributed to the lower electronegativity and higher basicity of the trimethylphosphine ligands in the complex $ReCl(CO)(PMe_3)_4$ as compared to that of the triphenylphosphine ligands in $ReCl_2(CO)_2(PPh_3)_2$.

The complex $ReCl(CO)(PMe_3)_4$ appears to be rather stable under dry nitrogen and in air for a period of several months. The complex only darkens slightly due to very slow decomposition in air over the course of four to six months.

One highly speculative possibility is that polymerization of the monomer $ReCl(CO)(PMe_3)_4$ via hydrido bridges could produce a polymer that is indefinitely stable in air. This type of material would have ultra-high tensile strength and ductility due to the stability provided by the hydrido bridges. This type of polymeric material could find potential use as a surfactant and/or coating. Further research in this area of organometallic polymerization has yet to be performed.

The proposed structure of such a polymer, with monomeric subunits of configuration $ReCl(CO)(PMe_3)_4$, is illustrated in Figure 16.

I. LITERATURE CITED:

1) F.A. Cotton and C.S. Kraihanzel, Inorg. Chem., **2**, 533 (1963).

2) F.A. Cotton, Inorg. Chem., **3**, 702 (1964).

3) F.A. Cotton and R.M. Wing, Inorg. Chem., **4**, 314 (1965)

4) T.A. Stephenson and G. Wilkinson, J. Inorg. Nuclear Chem., **28**, 1945 (1966).

5) D.D. Brown, C.K. Ingold, and R.S. Nyholm, J. Chem. Soc., 2674, 2680, 2696 (1953).

6) W. Hieber and W. Freyer, Chem. Ber., **93**, 462 (1960).

7) P.W. Jolly and F.G.A. Stone, J. Chem. Soc., 5259 (1965).

8) B.M. Mikhailov and N.F. Kucherova, Dokl. Akad. Nauk. SSSR, **74**, 501 (1950).

9) J.L. Willians, Chem. Ind. (London), 235 (1957).

10) H. Gilman, Ber. 61B, 907-11 (1928).

11) H. Zakharkin, B. Okhlobystin, and C. Strunin, Izv. Akad. Nauk SSSR, Old. Khim. Nauk, 2002-8 (1962).

12) E.W. Washburn and J.W. Read, J. Am. Chem. Soc., **41**, 729 (1919).

13) G.M. Kosolapoff, Organophosphorus Compounds, John Wiley and Sons, Inc., New York, p. 98, (1950).

14) G.M. Kosolapoff, Organophosphorus Compounds, John Wiley and Sons, Inc., New York, p. 10, (1950).

15) M.L. Kabachnik and E.S. Shepleva, Izv. Akad. Nauk. SSSR, Old. Khim. Nauk, No.1, **56**, (1949).

16) M.S. Kharasch, E.V. Jensen and S. Weinhouse, J. Org. Chem., **14**, 429 (1949).

17) M.H. Beeby and F.G. Mann, J. Chem. Soc., 411 (1951).

18) C. Stuebe, W.M. LeSuer and G.R. Norman, J. Amer. Chem. Soc., **77**, 3526 (1955); G.W. Parshall, J. Inorg. Nucl. Chem., **12**, 372 (1960).

19) Remy', H. Treatise on Inorganic Chemistry (translated and amended by J.S. Anderson), Vol. II, Elsevier, Amsterdam, (1956).

20) F. Albert Cotton, G. Wilkinson. Advanced Inorganic Chemistry- A Comprehensive Text, Interscience Publishers, p. 800-811, (1962).

21) Edwin M. Larsen. Transitional Elements, W.A. Benjamin, Inc., p. 125-154; (1965).

22) S.C. Abrahams, A.P. Ginsberg and K. Knox, Inorg. Chem. **3**, 528 (1964).

23) I. and W. Noddack. Z. anorg. chem., **215**, 146 (1933).

24) Woolf, A.A., Quart. Revs. (London), **15**, 372 (1962).

25) Edmund M. Wise. Palladium- Recovery, Properties, and Uses, Academic Press, p. 21-28, 29-91, 121-123; (1968)

26) F.A. Lewis. The Palladium/Hydrogen System, Academic Press, p. 133-149, 152-156; (1967).

27) Georg Brauer. Handbook of Preparative Inorganic Chemistry- Volume II, Second Edition, Academic Press, p. 1400; (1965).

28) M. Clyde Day, Jr. and Joel Selbin. Theoretical Inorganic Chemistry, Second Edition, Van Nostrand Reinhold Co., p. 391-412; (1969).

29) Bailer, J.C., ed., The Chemistry of Coordination Compounds (American Chemical Society Monograph, No. 131), Rheinhold, New York, (1956).

30) L.E. Orgel, Inorg. Chem., **1**, 25 (1962).

31) R.B. King and F.G.A. Stone, J. Am. Chem. Soc., **82**, 4557 (1960).

32) Kazuo Nakamoto, Paul J. McCarthy, S.J. Spectroscopy and Structure of Metal Chelate Compounds, John Wiley and Sons, Inc., p. 73-141; (1968).

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

34) F.A. Cotton, Accounts Chem. Res., **2**, 240 (1969).

35) J.R. Ebner and R.A. Walton, Inorg. Chem., **14**, 1987 (1975).

36) F.A. Cotton, B.G. DeBoer, and M. Jeremic, Inorg. Chem., 1970, **9**, 2143 (1970).

37) D.G. Tisley and R.A. Walton, Inorg. Chem., **12**, 373 (1973).

38) F.A. Cotton, B.A. Frenz, and T.R. Webb, J. Am. Chem. Soc., **95**, 4431 (1973); C.L. Angell, F.A. Cotton, B.A. Frenz, and T.R. Webb, J.C.S. Chem. Comm., 399 (1973).

39) F.A. Cotton, Inorg. Chem., **4**, 334 (1965); F.A. Cotton and C.B. Harris, ibid., **6**, 924 (1967).

40) F.A. Cotton, Acc. Chem. Res., **11**, 225 (1978).

41) F.A. Cotton, B.A. Frenz, B.R. Stults, and T.R. Webb, J. Am. Chem. Soc., **98**, 2768 (1976).

42) W.C. Trogler, E.I. Solomon, I. Trajberg, C.J. Ballhausen, and H.B Gray, Inorg. Chem., **16**, 828 (1977).

43) D.J. Salmon and R.A. Walton, J. Am. Chem. Soc., **100**, 991 (1978).

44) C.A. Hertzner and R.A. Walton, J. Organomet. Chem., **124**, C15 (1977).

45) J. Chatt, G.J. Leigh, and D.M.P. Minges, J. Am. Chem. Soc., **A**, 1674 (1969).

46) C.F.J. Barnard, J.A. Daniels, J. Jeffrey, and R.J. Mawby, J. Chem. Soc., Dalton Trans., 953 (1976).

47) G.L. Geoffroy, H.B. Gray, and G.S. Hammond, J. Am. Chem. Soc., **96**, 5565 (1974).

48) F.A. Cotton, L.W. Shive, and B.R. Stults, Inorg. Chem., **15**, 2239 (1976).

49) W.C. Trogler, C.D. Cowman, H.B. Gray, and F.A. Cotton, J. Am. Chem. Soc., **99**, 2993 (1977).

50) C. Tegner, Acta. Chem. Scand., **6**, 782 (1952).

51) A.D. Hamer, D.G. Tisley, and R.A. Walton, J. Inorg. Nucl. Chem., **36**, 1771 (1984).

52) L.H. Jones. *Advances in the Chemistry of the Coordination Compounds*, S. Kirschner, ed., The MacMillan Co., New York, N.Y., p. 398-411; (1961).

53) G. Booth, Adv. Inorg. Chem. Radiochem., **6**, 1 (1964).

54) S. Montelatici, A. vander Ent, J.A. Osborn, and G. Wilkinson, J. Chem. Soc. **A**, 1657 (1968).

55) P.S. Hallman, D. Evans, J.A. Osborn, and G. Wilkinson, Chem. Comm., 305 (1967).

56) M.L. Maddox, J.L. Stafford, and H.D. Kaesz, Adv. Organometallic Chem., **3**, 1 (1963).

57) M.H.B. Stiddard, J. Chem. Soc., 756 (1963).

58) R.J. Angelici and J.R. Graham, J. Am. Chem. Soc., **87**, 5586 (1965).

Appendix A - Tables

Table I

Infrared Vibrational Frequencies for Phosphine Complexes of the type, ReCl$_2$(CO)$_2$(PR$_3$)$_2$*

Complex	Medium	Intensity	IR vibrational band (cm^{-1})	
ReCl$_2$-(CO)$_2$-(PR$_3$)$_2$	C_6H_6	vw	5000	
		w	4550	
		m	4525	
		vw	4510	
		vw	4000	
		w	3950	
		w	3875	
		m	3800	
		s	3400	
		vw	3000	
		vw	2950	
		m	2200	
		vs	1910	(-C≡O)
		vw	1750	
		s	1700	
		vw	1000	
		s	800	(doublet)
		w	600	
		w	500	
		s	315	

* PR$_3$ indicates PPh$_3$, PEt$_3$, PPr$_3$

Table II

Infrared Vibrational Frequencies of Triphenylphosphine

Species	Medium	Intensity	IR vibrational band (cm^{-1})
Prepared crystals	CS_2	vs	2950
		m	2150
		s	1975
		s	1825
		s	1800
		m	1600
		m	1360
		s	1310 (doublet)
		m	1260
		s	1170
		m	1080
		vs	1060
		s	1010
		vw	980
		s	920
		m	850
		vs	750
Triphenylphosphine	CS_2	vs	3000
		m	2250
		s	1945
		s	1860
		s	1810
		m	1650
		m	1370
		s	1300 (doublet)
		m	1270
		s	1180
		vs	1060
		s	985
		s	908
		m	840
		vs	700

Table III

Bonding in Metal Carbonyls

Group	Symmetry Type	Orbitals	Bonding Type
I	A_{1g}	s	σ
	E_{1g}	$d_{x^2}, d_{x^2-y^2}$	σ
II	T_{2g}	d_{xz}, d_{yz}, d_{xy}	π
III	T_{1u}	p_x, p_y, p_z	σ or π

Table IV

Secular Equations and Related Information on CO* Stretching Modes

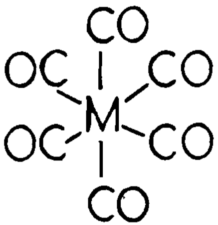
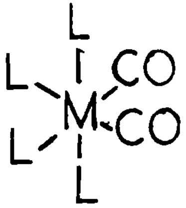
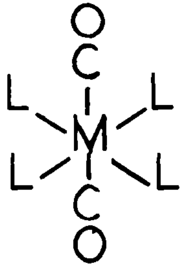
molecular type	molecular symmetry	symmetry species	activities	secular equations
$M(CO)_6$	O_h	A_{1g}	Raman	$\lambda = \mu(K + K_t + 4K_c)$
		E_g	Raman	$\lambda = \mu(K + K_t - 2K_c)$
		T_{1u}	Infrared	$\lambda = \mu(K - K_t)$
		A_1^1	Infrared and Raman	$\begin{vmatrix} \mu K_1 - \lambda & \mu K_c \\ 2\mu K_c & \mu(K_2 + K_t + 2K_c') - \lambda \end{vmatrix}$
		A_1^2	Raman	
		B_1	Infrared	$\lambda = \mu(K_2 + K_t - 2K_c')$
		E	Raman	$\lambda = \mu(K_2 - K_t)$

Table IV (cont)

molecular type	molecular symmetry	symmetry species	activities	secular equations
cis-$ML_4(CO)_2$		A_1	Infrared	$\lambda = \mu(K + K_c)$
	C_{2v}	B_1	Raman	$\lambda = \mu(K - K_c)$
trans-$ML_4(CO)_2$		A_{1g}	Raman	$\lambda = \mu(K + K_t)$
	D_{4h}	A_{2u}	Infrared	$\lambda = \mu(K - K_t)$

---

* Force constants in mdyne/Å, μ represents the reciprocal of the reduced mass of the CO oscillater, $\lambda = (5.8890 \times 10^{-2})\nu^2$, where ν^2 is the frequency in cm^{-1}

Table V

Infrared Vibrational Frequencies for the Prepared Complex $ReCl_2(CO)_2(PPh_3)_2$ in Pure Benzene Solvent

Complex	Medium	Intensity	IR vibrational band (cm^{-1})
$ReCl_2$- $(CO)_2$- $(PPh_3)_2$	C_6H_6	w	4650
		vw	4500
		w	4225
		s	4100
		vw	3950
		vw	3700
		vw	3300
		m	3250
		s	3100
		vw	2710
		w	2625
		m	2500
		vw	2275
		m	2100
		vs	1906 $(\cdot C\equiv O)$
		vw	1900
		vw	1850
		s	1600
		vw	1450
		s	1350
		s	1300w

Table VI

Force Constants Obtained with the CO Assignment in $ReCl_2(CO)_2(PPh_3)_2$*

Complex	Assignment	Calculated Force Constants	
		k_t	k_i
trans-$ReCl_2(CO)_2$-$(PPh_3)_2$	A_{2u} 1906	13.82	0.88
cis-$ReCl_2(CO)_2$-$(PPh_3)_2$	A_1 1906	Imaginary roots obtained	

---

* Force constants are in mdyne/Å, and assignment frequencies are in cm^{-1}.

Table VII

Infrared Vibrational Frequencies for the Prepared Complex, $ReCl(CO)(PMe_3)_4$ in Benzene Solvent

Complex	Medium	Intensity	IR vibrational band (cm^{-1})
$ReCl(CO)(PMe_3)_4$	C_6H_6	vw	4900
		w	4700
		w	4600
		m	4300
		s	3950
		s	3500
		s	3300
		m	3000
		m	2850
		vw	2550
		s	2225
		vs	1780 $(\cdot C\equiv O)$
		s	1000
		s	900
		vs	800

Table VIII

Infrared Vibrational Frequencies for Trimethylphosphine in Carbon disulfide Solvent

Complex	Medium	Intensity	IR vibrational band (cm^{-1})
Trimethylphosphine	CS_2	w	4800
		vw	4650
		w	4450
		w	4025
		vw	3950
		m	3700
		vs	3000
		w	2700
		w	2550
		vw	2300
		m	2200
		vw	1700
		m	1525
		s	1300
		s	1100
		s	850
		vs	700

Table VIII

Infrared Vibrational Frequencies for Trimethylphosphine in Carbon disulfide Solvent

Complex	Medium	Intensity	IR vibrational band (cm^{-1})
Trimethyl-phosphine	CS_2	w	4800
		vw	4650
		w	4450
		w	4025
		vw	3950
		m	3700
		vs	3000
		w	2700
		w	2550
		vw	2300
		m	2200
		vw	1700
		m	1525
		s	1300
		s	1100
		s	850
		vs	700

Table IX

Boiling Point Data for Pure Benzene Solvent
Temperature (°C) vs. Time (min)

Solvent	Temperature (°C)	Time (min)
Benzene	24.9	0
	25.2	0.5
	26.1	1.0
	27.3	1.5
	28.2	2.0
	28.9	2.5
	30.1	3.0
	34.0	3.5
	39.5	4.0
	50.0	4.5
	70.0	5.0
	78.2	5.5
	79.5	6.0
	79.5	6.5
	79.5	7.0
	79.5	7.5
	79.3	8.0
	79.1	8.5
	78.8	9.0
	78.5	9.5
	78.0	10.0

Table X

Boiling Point Data for a 0.00435 m Solution of Triphenylphosphine in Pure Benzene Solvent
(Temperature (°C) vs. Time (min)

Solution	Temperature (°C)	Time (min)
Triphenylphosphine/Benzene	23.0	0
	25.1	0.5
	25.9	1.0
	26.0	1.5
	26.5	2.0
	27.2	2.5
	28.4	3.0
	32.0	3.5
	46.2	4.0
	65.3	4.5
	79.2	5.0
	82.9	5.5
	82.5	6.0
	81.5	6.5
	81.5	7.0
	81.0	7.5
	80.8	8.0
	80.5	8.5
	80.2	9.0
	80.0	9.5
	80.0	10.0

Table XI

Boiling Point Data for a 0.00399 m Solution of $ReCl_2(CO)_2(PPh_3)_2$ in Pure Benzene Solvent

Temperature (°C) vs. Time (min)

Solution	Temperature (°C)	Time (min)
$ReCl_2(CO)_2(PPh_3)_2$/Benzene	24.5	0
	24.9	0.5
	25.3	1.0
	25.9	1.5
	26.7	2.0
	30.9	2.5
	34.6	3.0
	40.5	3.5
	49.3	4.0
	73.5	4.5
	80.9	5.0
	80.9	5.5
	80.7	6.0
	80.7	6.5
	80.7	7.0
	80.7	7.5
	80.5	8.0
	80.0	8.5
	80.0	9.0
	79.5	9.5
	79.0	10.0

Table XII

Boiling Point Data for Pure Diethyl Ether Solvent (Temperature (°C) vs. Time (min)

Solvent	Temperature (°C)	Time (min)
Diethyl Ether	24.0	0
	29.7	0.5
	31.5	1.0
	32.0	1.5
	33.8	2.0
	34.0	2.5
	34.2	3.0
	34.5	3.5
	34.5	4.0
	34.5	4.5
	34.2	5.0
	34.0	5.5
	34.0	6.0
	34.0	6.5
	33.5	7.0
	33.5	7.5
	33.0	8.0
	33.0	8.5
	32.5	9.0
	32.5	9.5
	32.0	10.0

Table XIII

Boiling Point Data for a 0.0381 m Solution of Trimethylphosphine in Diethyl Ether Solvent (Temperature (°C) vs. Time (min))

Solution	Temperature (°C)	Time (min)
Trimethylphosphine/ Diethyl Ether	23.0	0
	24.1	0.5
	24.5	1.0
	25.0	1.5
	25.5	2.0
	26.9	2.5
	30.8	3.0
	34.3	3.5
	34.9	4.0
	34.9	4.5
	34.9	5.0
	34.5	5.5
	34.5	6.0
	34.0	6.5
	34.0	7.0
	33.4	7.5
	33.4	8.0
	32.8	8.5
	32.5	9.0
	32.0	9.5
	31.3	10.0

Table XV

Boiling Point Data for a 0.00275 m Solution of $ReCl(CO)(PMe_3)_4$ in Methylene Chloride Solvent

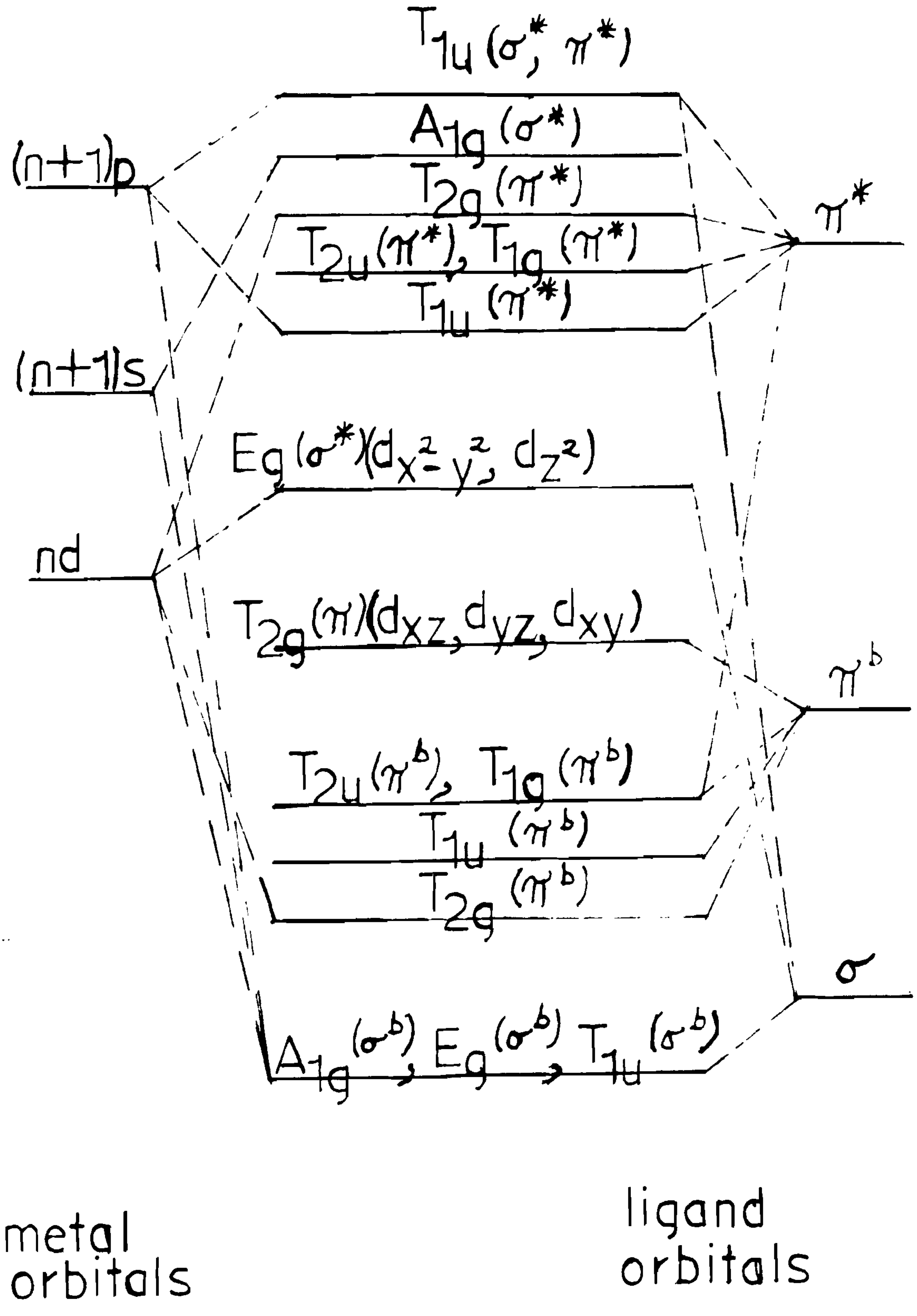
(Temperature (°C) vs. Time (min))

Solution	Temperature (°C)	Time (min)
$ReCl(CO)(PMe_3)_4$/ Methylene chloride	25.1	0
	25.9	0.5
	26.7	1.0
	27.5	1.5
	30.6	2.0
	33.5	2.5
	35.9	3.0
	37.3	3.5
	39.5	4.0
	41.0	4.5
	41.0	5.0
	41.0	5.5
	40.8	6.0
	40.0	6.5
	39.5	7.0
	39.0	7.5
	38.5	8.0
	37.9	8.5
	37.4	9.0
	36.8	9.5
	36.2	10.0

Appendix B - Figures

Figure 1

<u>Qualitative Molecular Orbital Schematic for a Substituted Metal Carbonyl</u>



T1u (σ*, π*)
A1g (σ*)
T2g (π*)
T2u (π*), T1g (π*)
T1u (π*)
(n+1)p
(n+1)s
Eg (σ*)(dx²-y², dz²)
nd
T2g (π)(dxz, dyz, dxy)
T2u (πb), T1g (πb)
T1u (πb)
T2g (πb)
A1g (σb), Eg (σb), T1u (σb)
π*
πb
σ
metal orbitals
ligand orbitals

Figure 2

Conversion of the Metal-Metal Bonded Dimer, $Re_2Cl_6(PR_3)_2$, by CO to the Dicarbonyl Monomer, $ReCl_2(CO)_2(PR_3)_2$

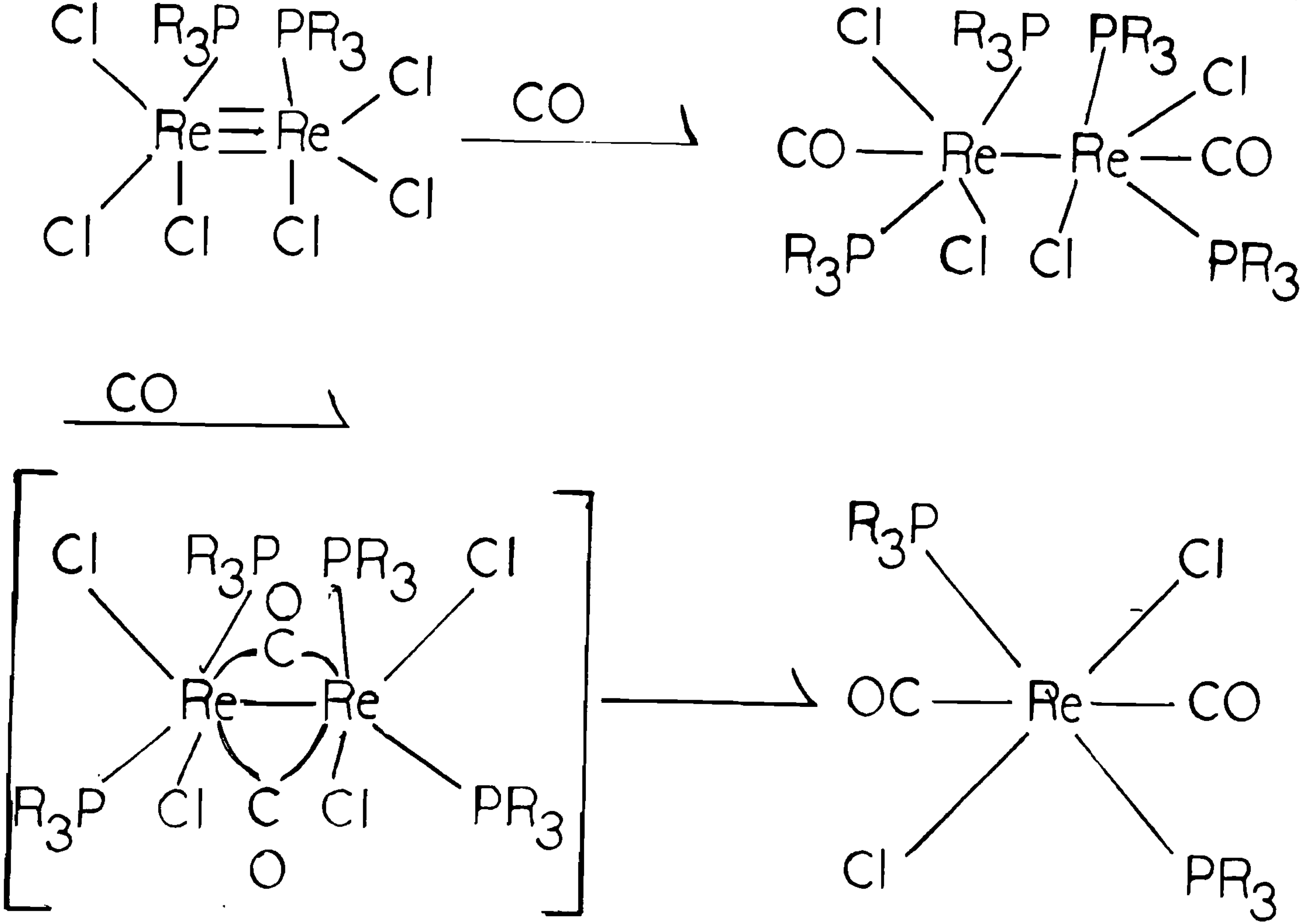

CO
CO

Figure 3

Heating Curve for Pure Benzene Solvent
Temperature (°C) vs. Time (min)

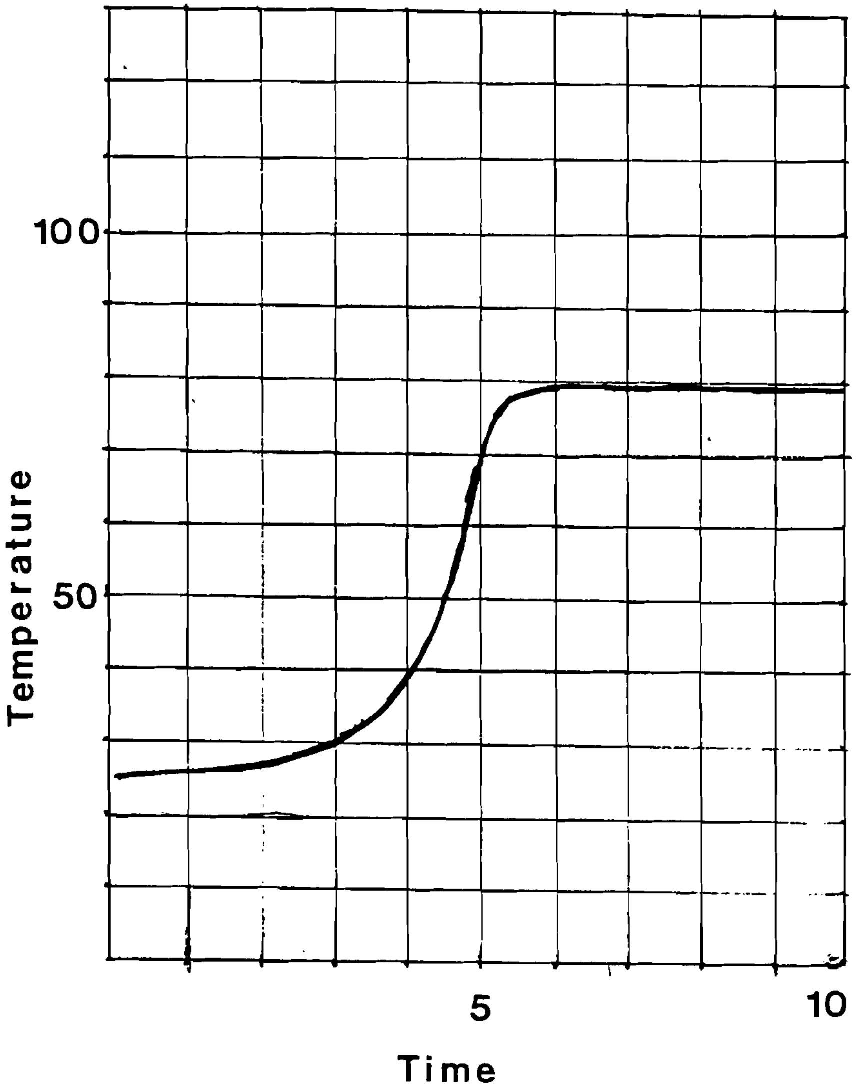

100
50
Temperature
5
10
Time

Figure 4

Heating Curve for a 0.00435 m Solution of Triphenylphosphine in Benzene Solvent Temperature (°C) vs. Time (min)

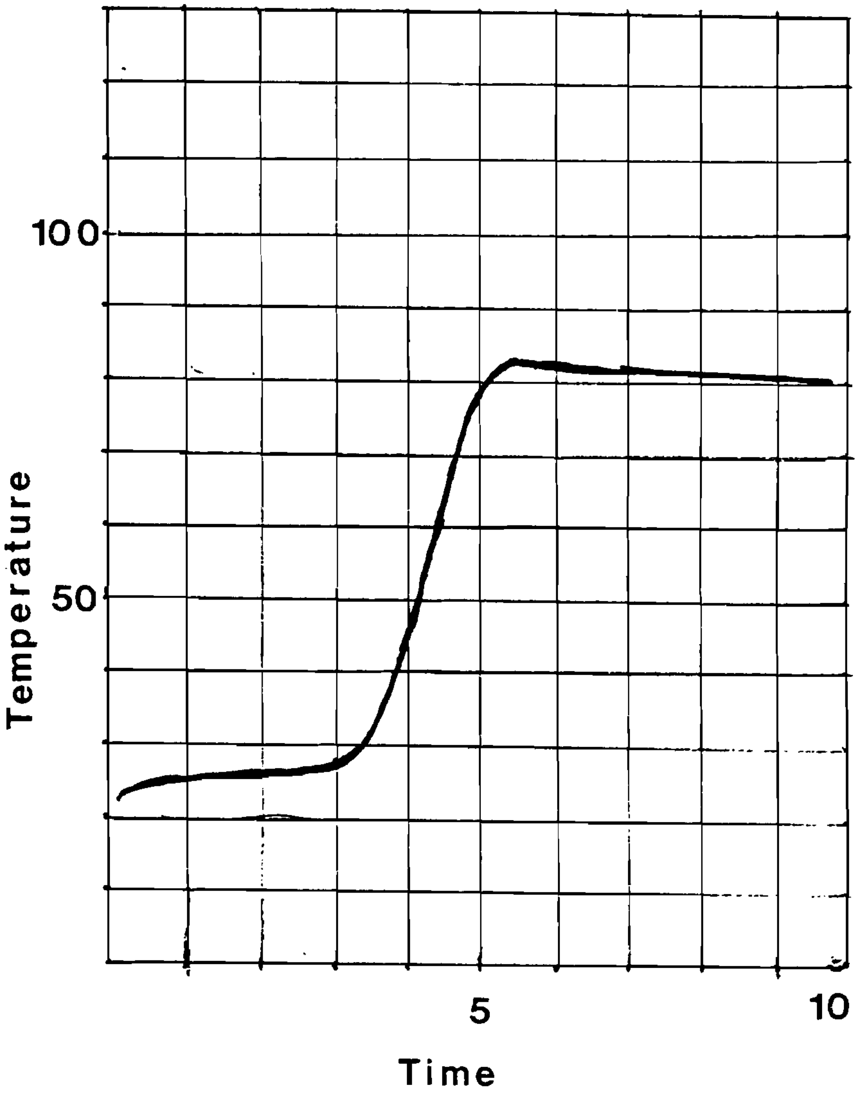

100
50
Temperature
5
10
Time

Figure 5

FT-IR spectrum of Triphenylphosphine in Carbon Disulfide Solvent

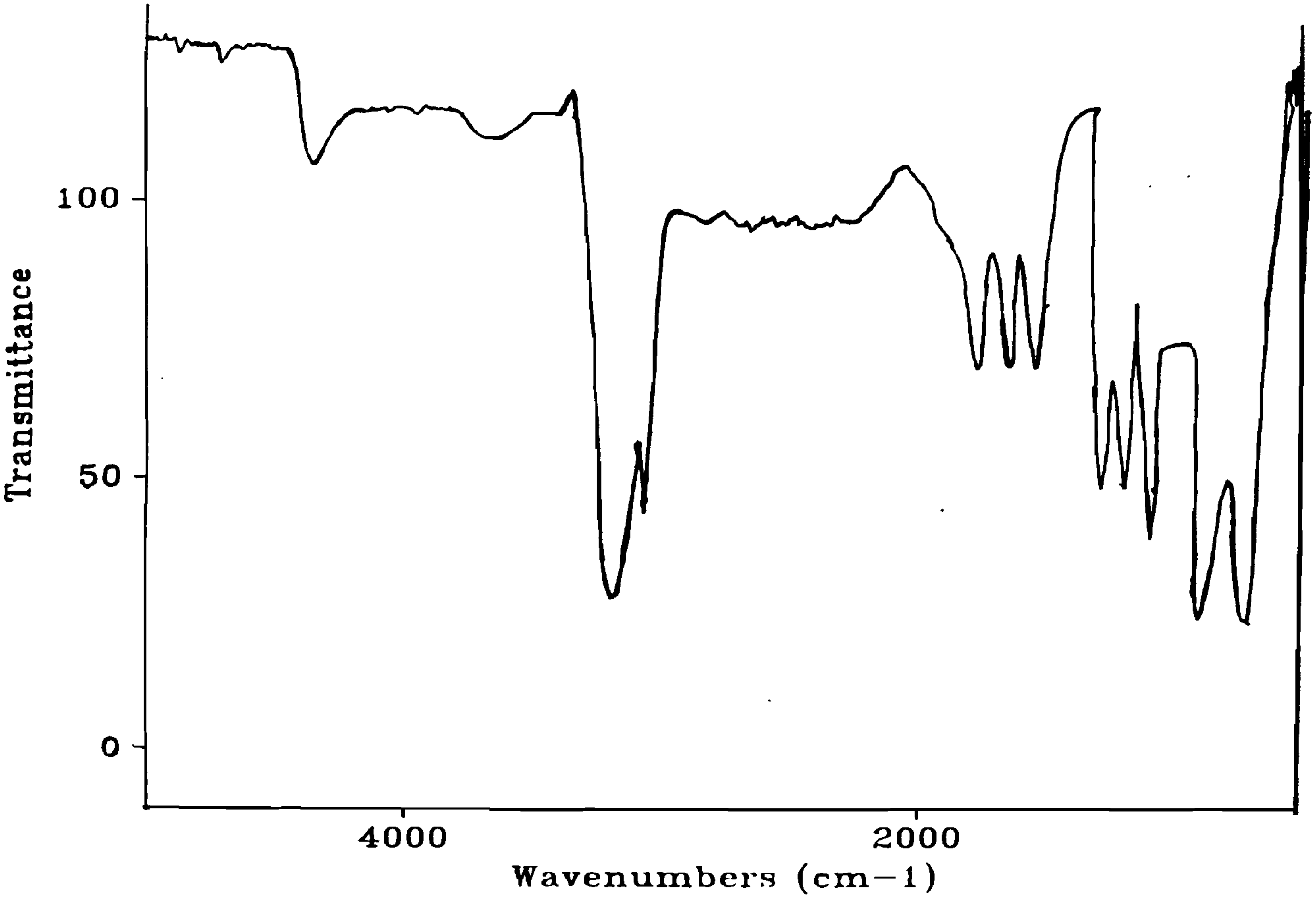

Transmittance
100
50
0
4000
2000
Wavenumbers (cm−1)

Figure 6

FT-IR Spectrum of Carbonylbis(triphenylphosphine)rhenium(II) Chloride in Benzene Solvent

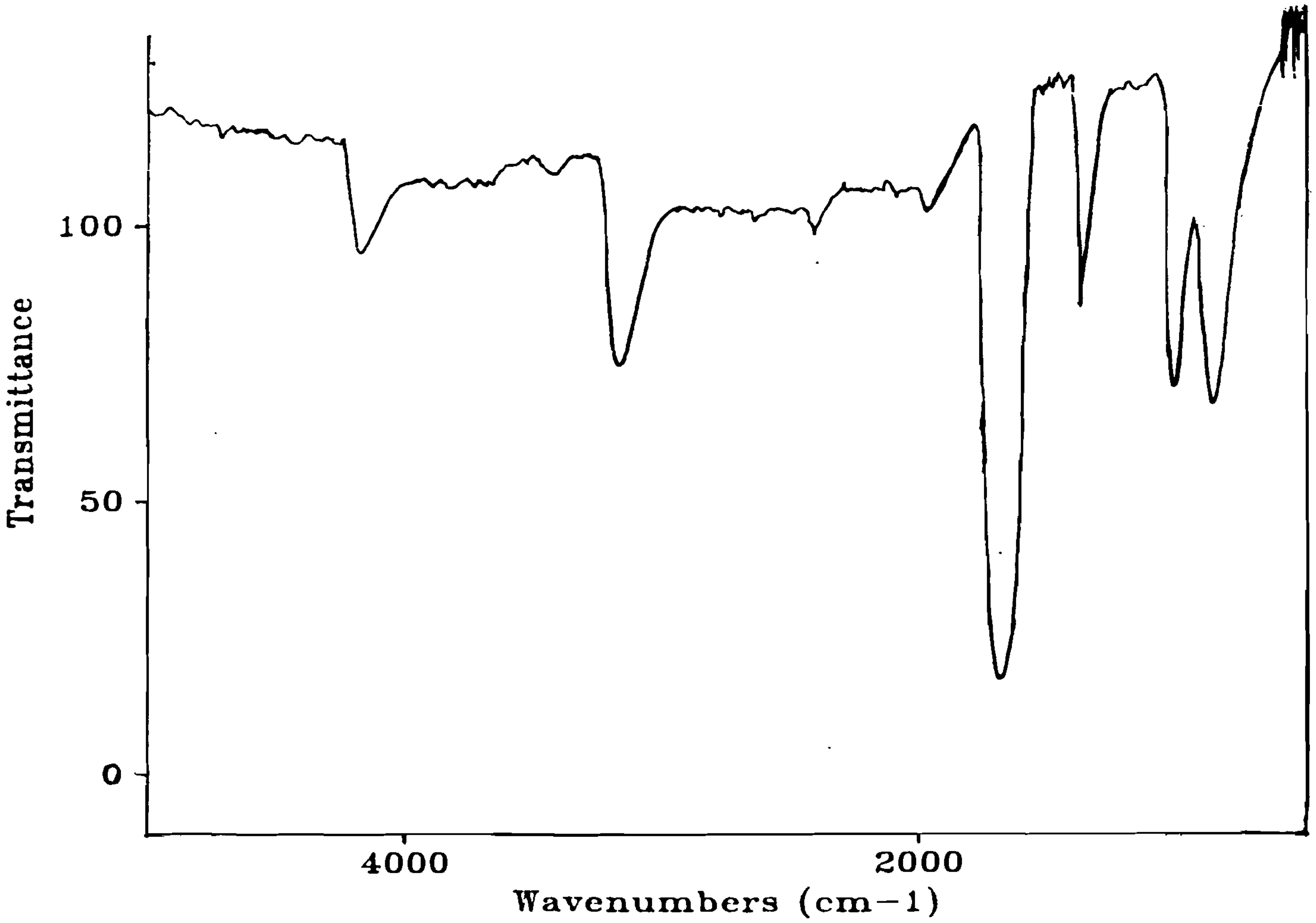

Transmittance
100
50
0
4000
2000
Wavenumbers (cm−1)

Figure 7

FT-IR Spectrum of Carbonylbis(triphenylphosphine)rhenium(II) Chloride in Benzene Solvent

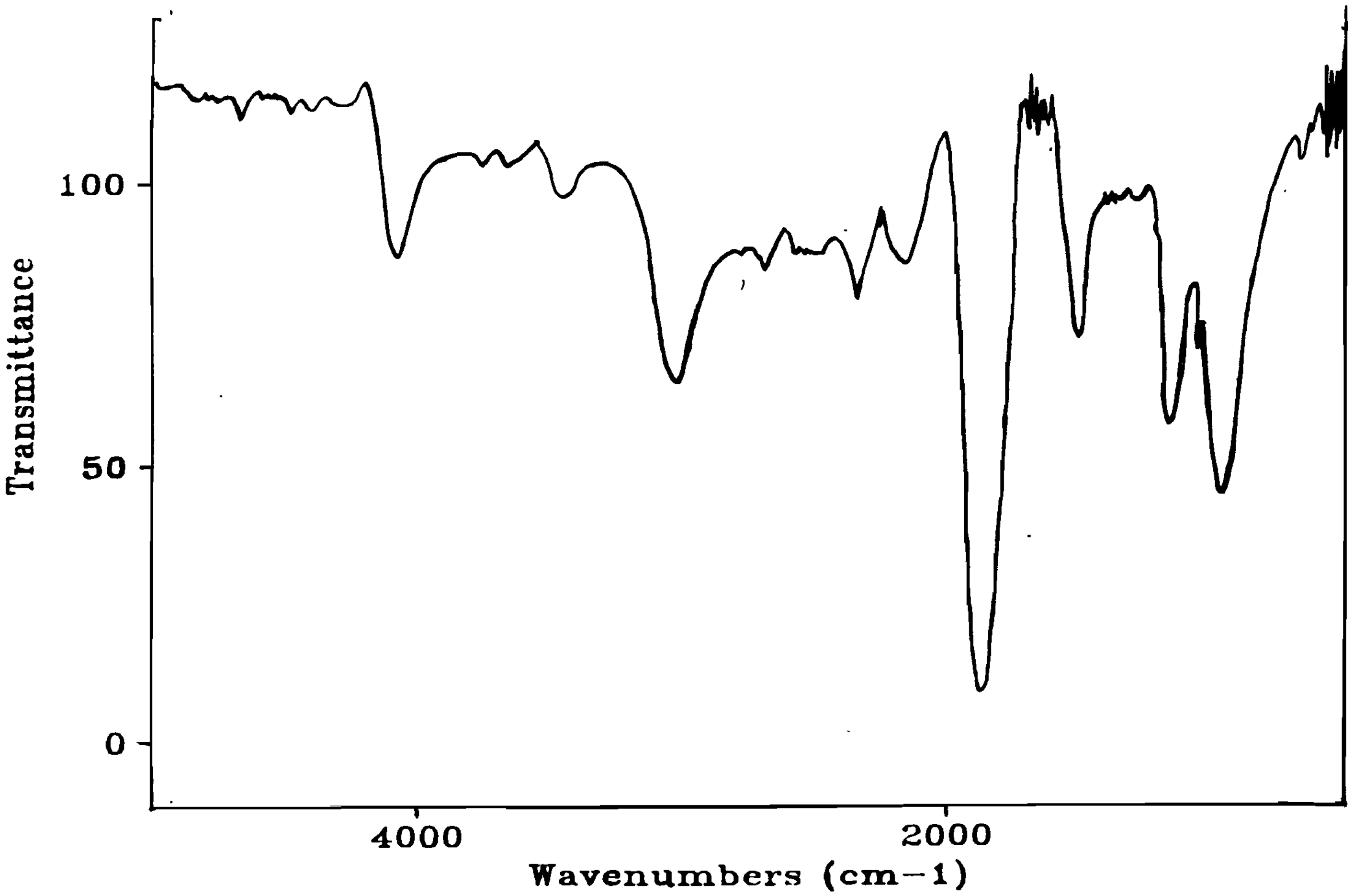

Transmittance
100
50
0
4000
2000
Wavenumbers (cm−1)

Figure 8

FT-IR Spectrum of Trimethylphosphine in Carbon Disulfide Solvent

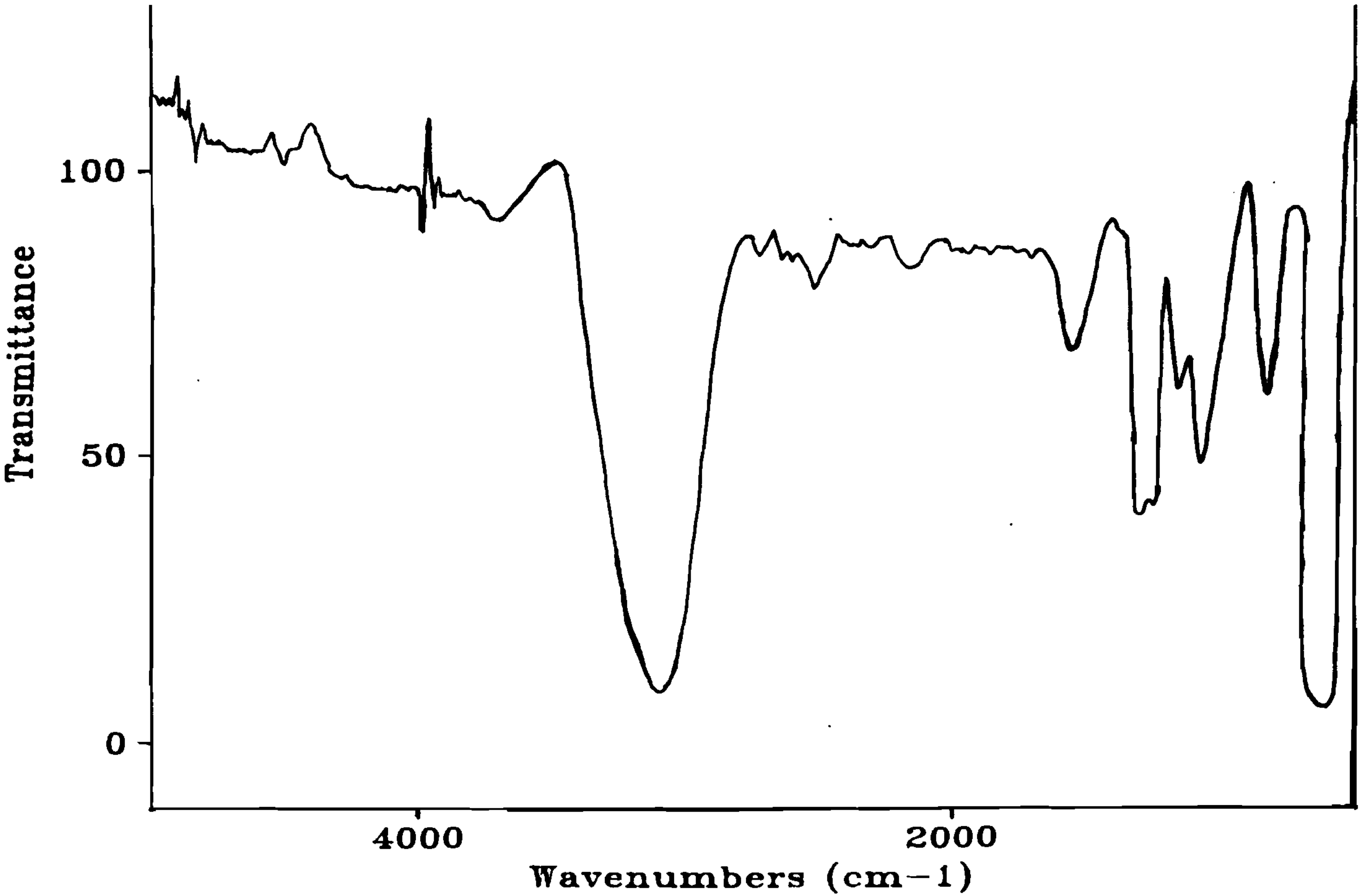

Transmittance
100
50
0
4000
2000
Wavenumbers (cm−1)

Figure 9

FT-IR Spectrum of Carbonyltetrakis(trimethylphosphine)rhenium(I) Chloride in Benzene Solvent

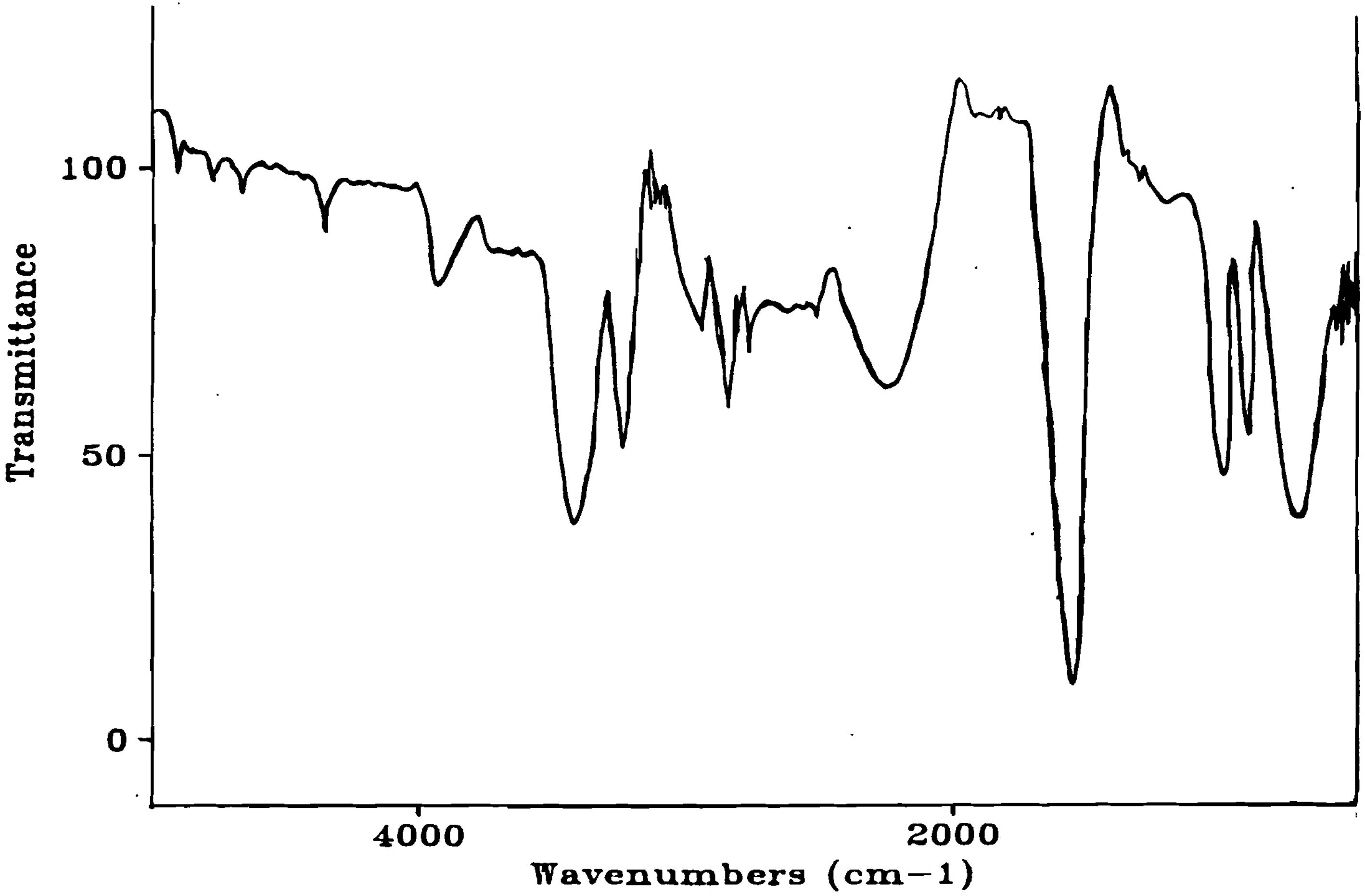

Transmittance
100
50
0
4000
2000
Wavenumbers (cm−1)

Figure 10

Proposed Qualitative Schematic for the Reaction of Rhenium(III) Tertiary Phosphine Complexes with N,N-Dimethylformamide

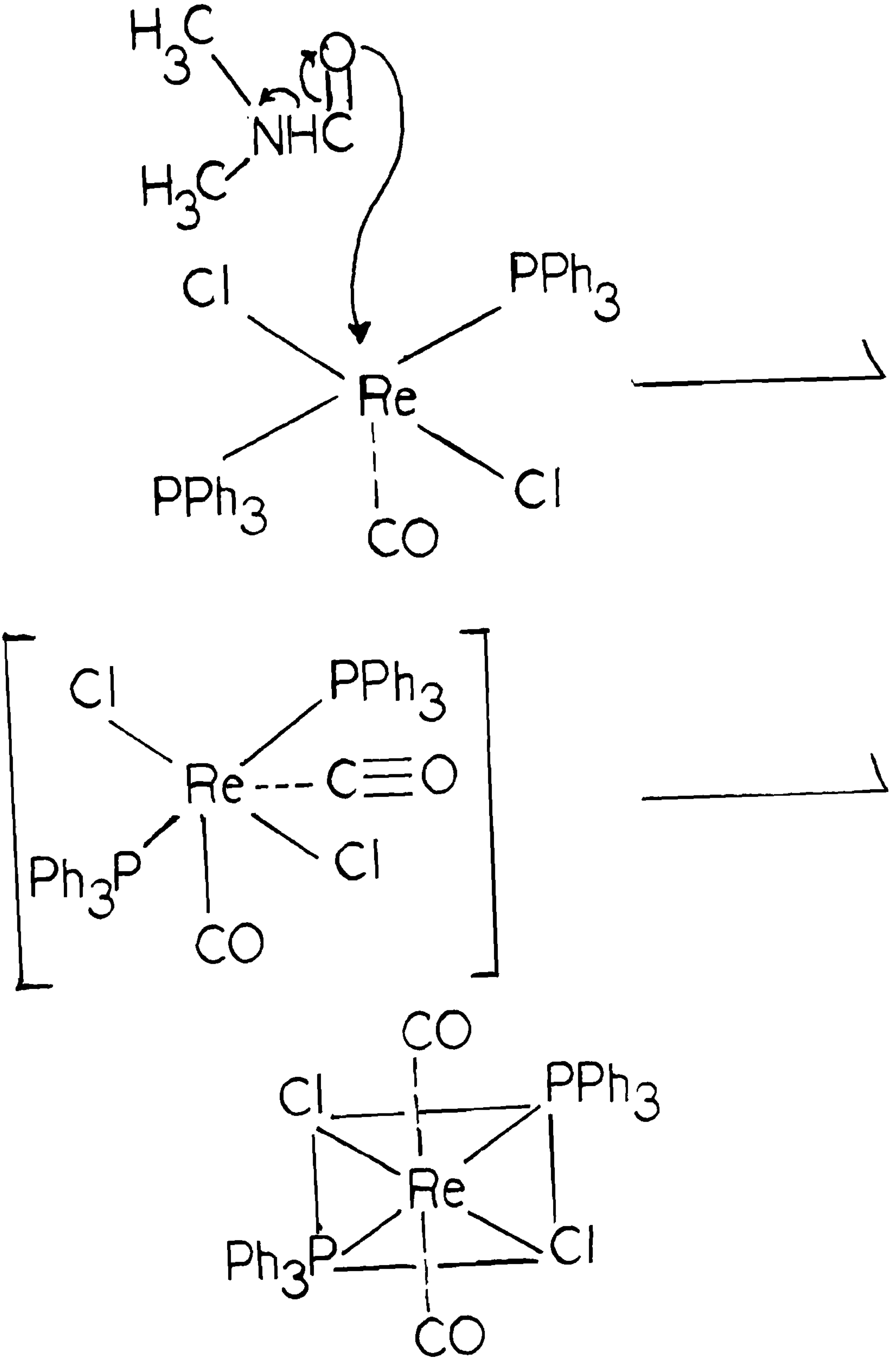

H_3C
H_3C
NHC
O
Cl
PPh_3
Re
PPh_3
CO
Cl
Cl
PPh_3
Re
C≡O
Ph_3P
Cl
CO
CO
Cl
PPh_3
Re
Ph_3P
Cl
CO

Figure 11

<u>Proposed Structure of Carbonylbis
(triphenylphosphine)
rhenium(II) Chloride</u>

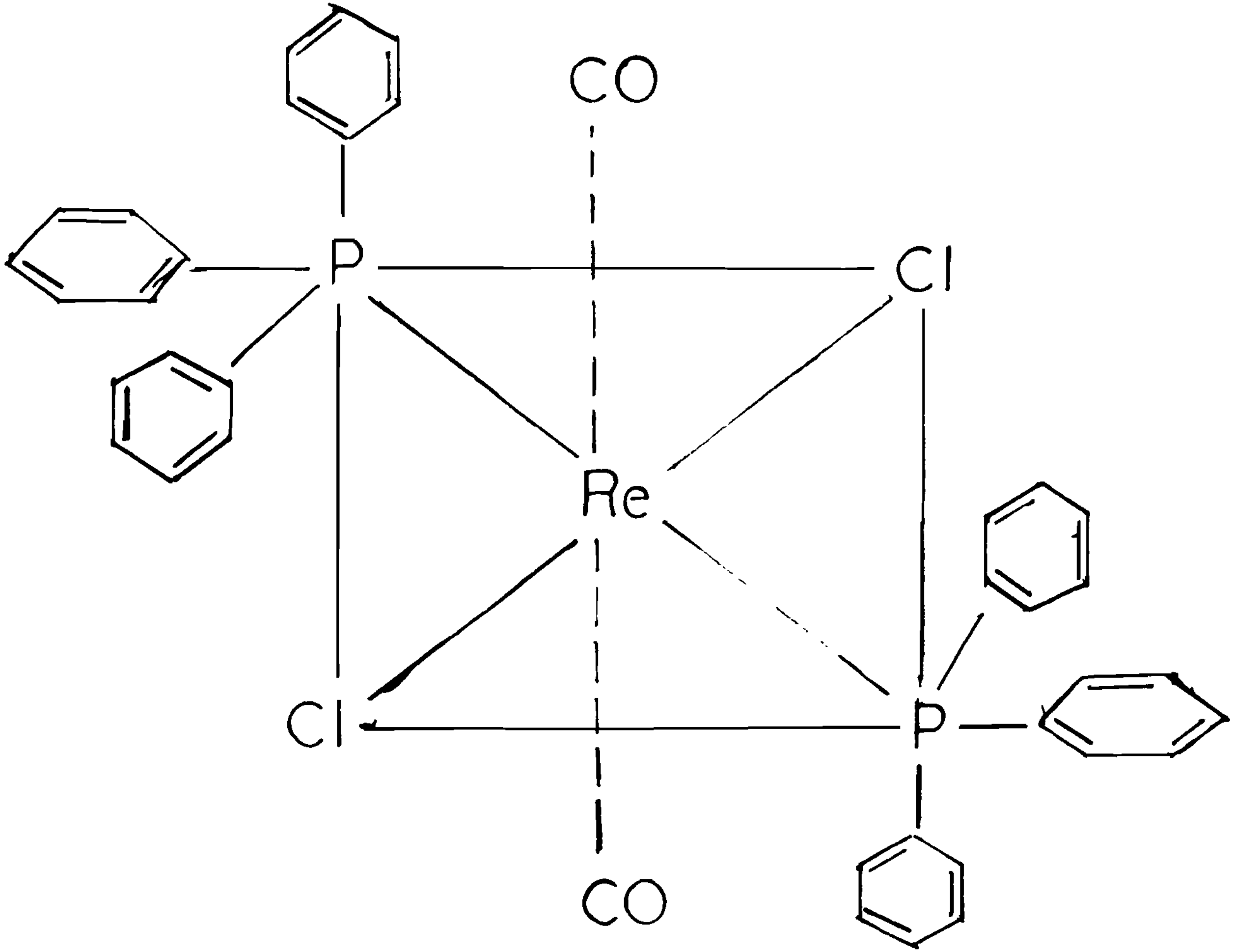

CO
P
Cl
Re
Cl
P
CO

Figure 12

Product Distributions for the Reaction of $Re_2Cl_2(PPh_3)_2$ with DMF in Refluxing Diglyme or 95% w/w Ethanol

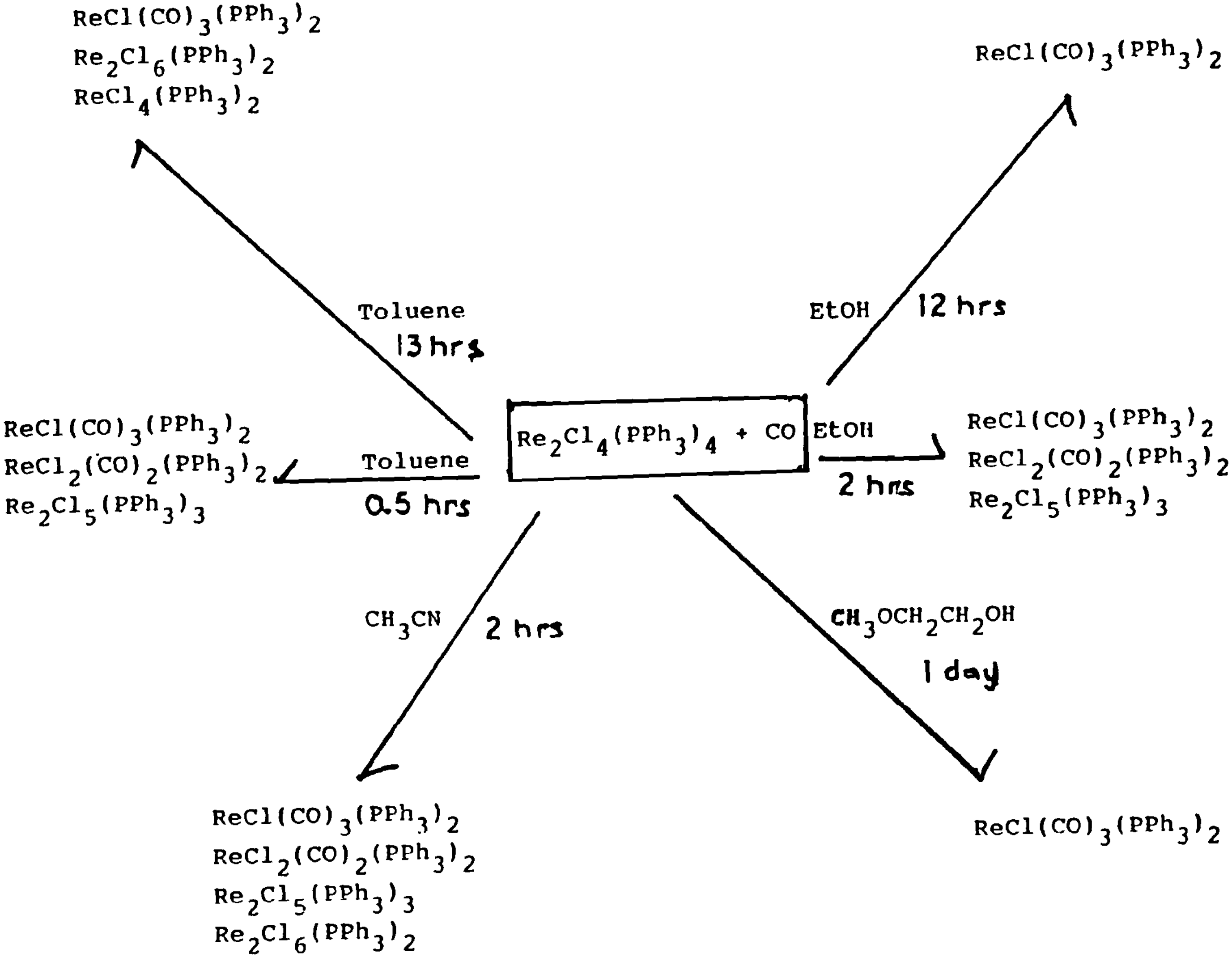
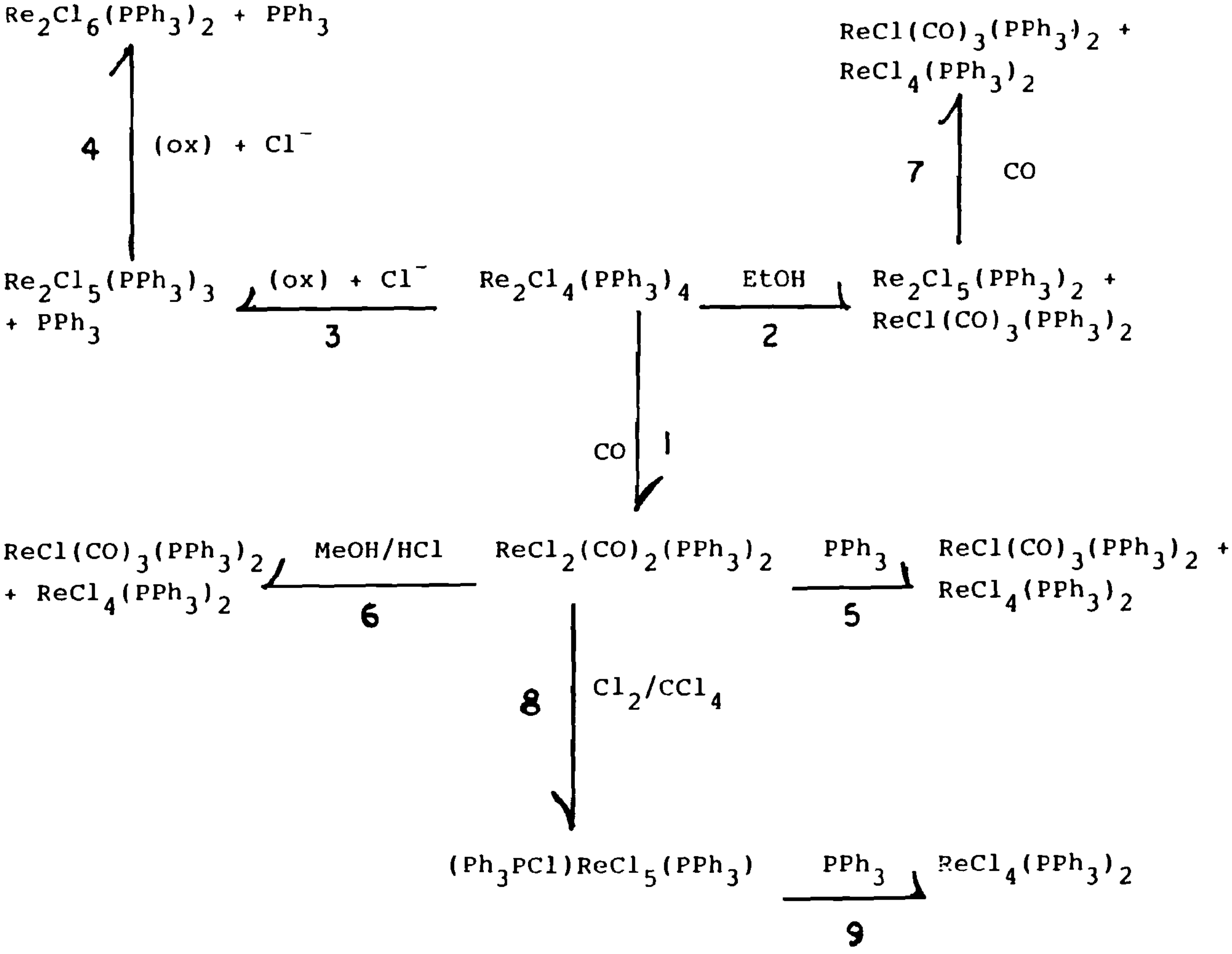

ReCl(CO)$_3$(PPh$_3$)$_2$
Re$_2$Cl$_6$(PPh$_3$)$_2$
ReCl$_4$(PPh$_3$)$_2$
Toluene
13 hrs
ReCl(CO)$_3$(PPh$_3$)$_2$
EtOH
12 hrs
ReCl(CO)$_3$(PPh$_3$)$_2$
ReCl$_2$(CO)$_2$(PPh$_3$)$_2$
Re$_2$Cl$_5$(PPh$_3$)$_3$
Toluene
0.5 hrs
Re$_2$Cl$_4$(PPh$_3$)$_4$ + CO
EtOH
2 hrs
ReCl(CO)$_3$(PPh$_3$)$_2$
ReCl$_2$(CO)$_2$(PPh$_3$)$_2$
Re$_2$Cl$_5$(PPh$_3$)$_3$
CH$_3$CN
2 hrs
CH$_3$OCH$_2$CH$_2$OH
1 day
ReCl(CO)$_3$(PPh$_3$)$_2$
ReCl$_2$(CO)$_2$(PPh$_3$)$_2$
Re$_2$Cl$_5$(PPh$_3$)$_3$
Re$_2$Cl$_6$(PPh$_3$)$_2$
ReCl(CO)$_3$(PPh$_3$)$_2$

Figure 13

Schematic Outlining the Probable Reactions Occuring in the $ReCl_2(PPh_3)_2$-CO System In Reactions 3 and 4, [ox] represents an oxidizing agent


$Re_2Cl_6(PPh_3)_2$ + PPh_3
4
(ox) + Cl^-
$ReCl(CO)_3(PPh_3)_2$ +
$ReCl_4(PPh_3)_2$
7
CO
$Re_2Cl_5(PPh_3)_3$
+ PPh_3
(ox) + Cl^-
3
$Re_2Cl_4(PPh_3)_4$
EtOH
2
$Re_2Cl_5(PPh_3)_2$ +
$ReCl(CO)_3(PPh_3)_2$
CO
1
$ReCl(CO)_3(PPh_3)_2$
+ $ReCl_4(PPh_3)_2$
MeOH/HCl
6
$ReCl_2(CO)_2(PPh_3)_2$
PPh_3
5
$ReCl(CO)_3(PPh_3)_2$ +
$ReCl_4(PPh_3)_2$
8
Cl_2/CCl_4
$(Ph_3PCl)ReCl_5(PPh_3)$
PPh_3
9
$ReCl_4(PPh_3)_2$

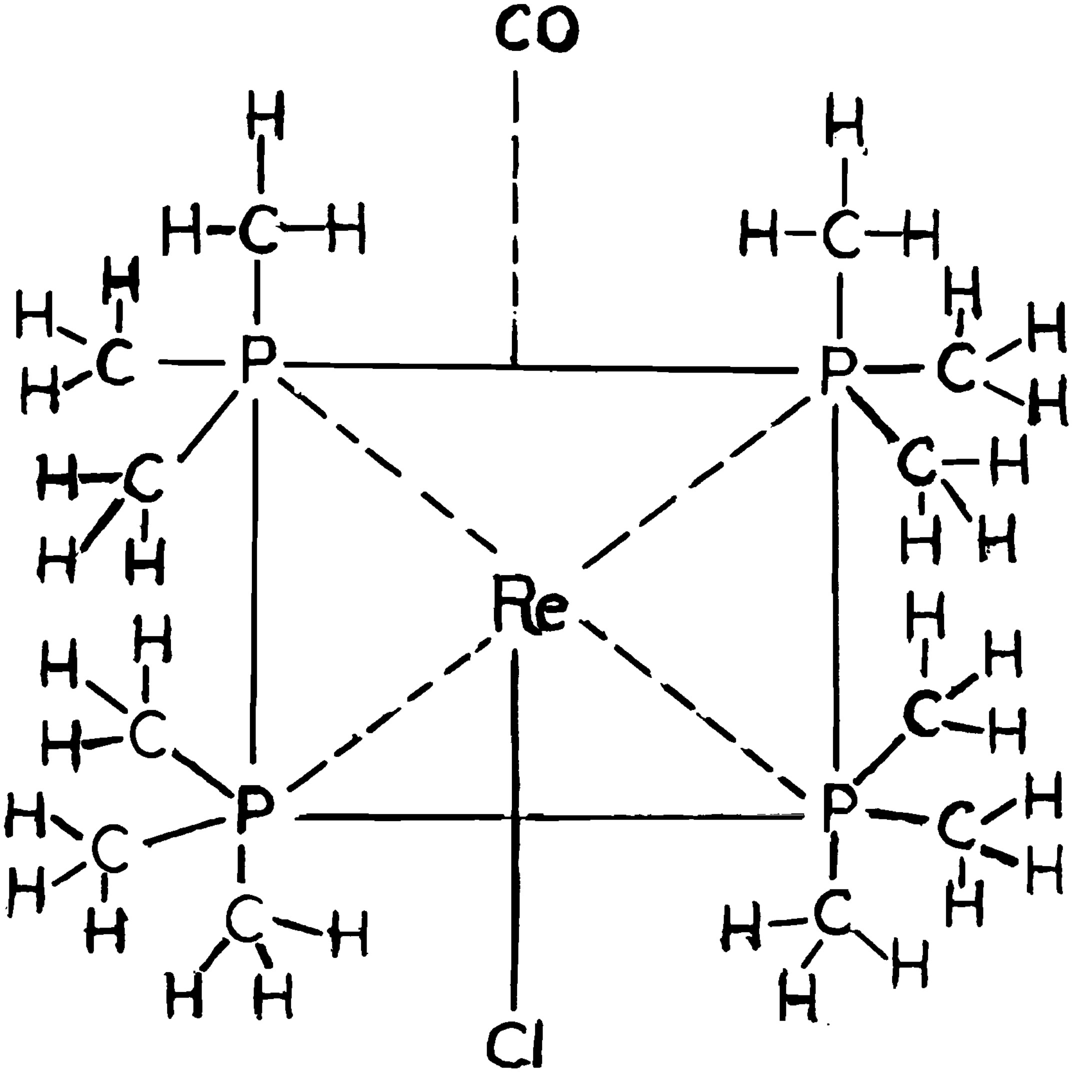

CO
Re
Cl
P
P
P
P
C
H

Figure 15

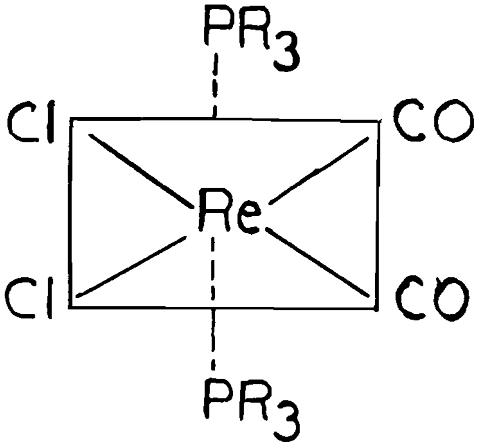
Possible Geometric Isomers of $ReCl_2(CO)_2(PR_3)_2$, Where R Indicates the Triphenylphosphine Ligand

I. cis-$ReCl_2(CO)_2(PR_3)_2$

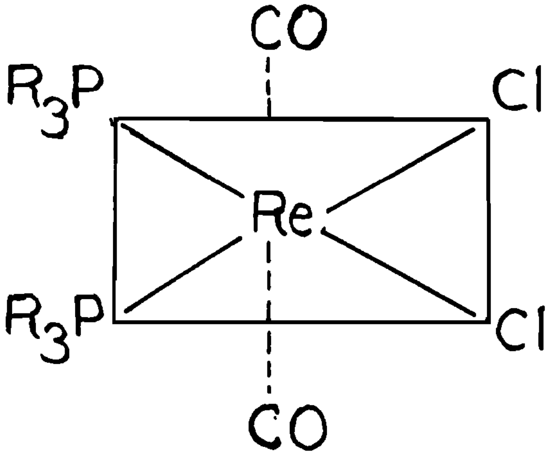
II. trans-$ReCl_2(CO)_2(PR_3)_2$

III. trans-dichloro, $ReCl_2(CO)_2(PR_3)_2$

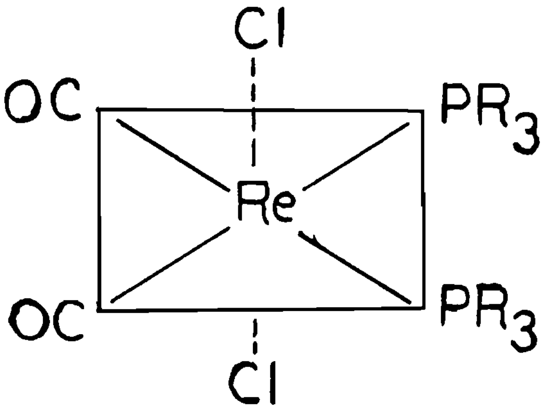
IV. cis-dichloro, $ReCl_2(CO)_2(PR_3)_2$


PR3
Cl
CO
Re
Cl
CO
PR3

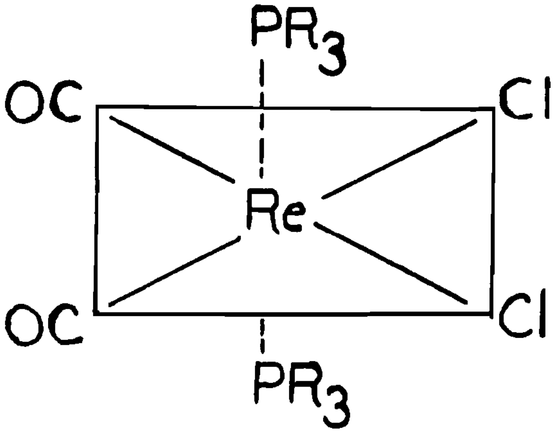
I


CO
R3P
Cl
Re
R3P
Cl
CO

II


Cl
OC
PR3
Re
OC
PR3
Cl

III


PR3
OC
Cl
Re
OC
Cl
PR3

IV

Figure 16

Proposed Structure of Polymeric Carbonyl tetrakis(trimethylphosphine) rhenium(I) Chloride

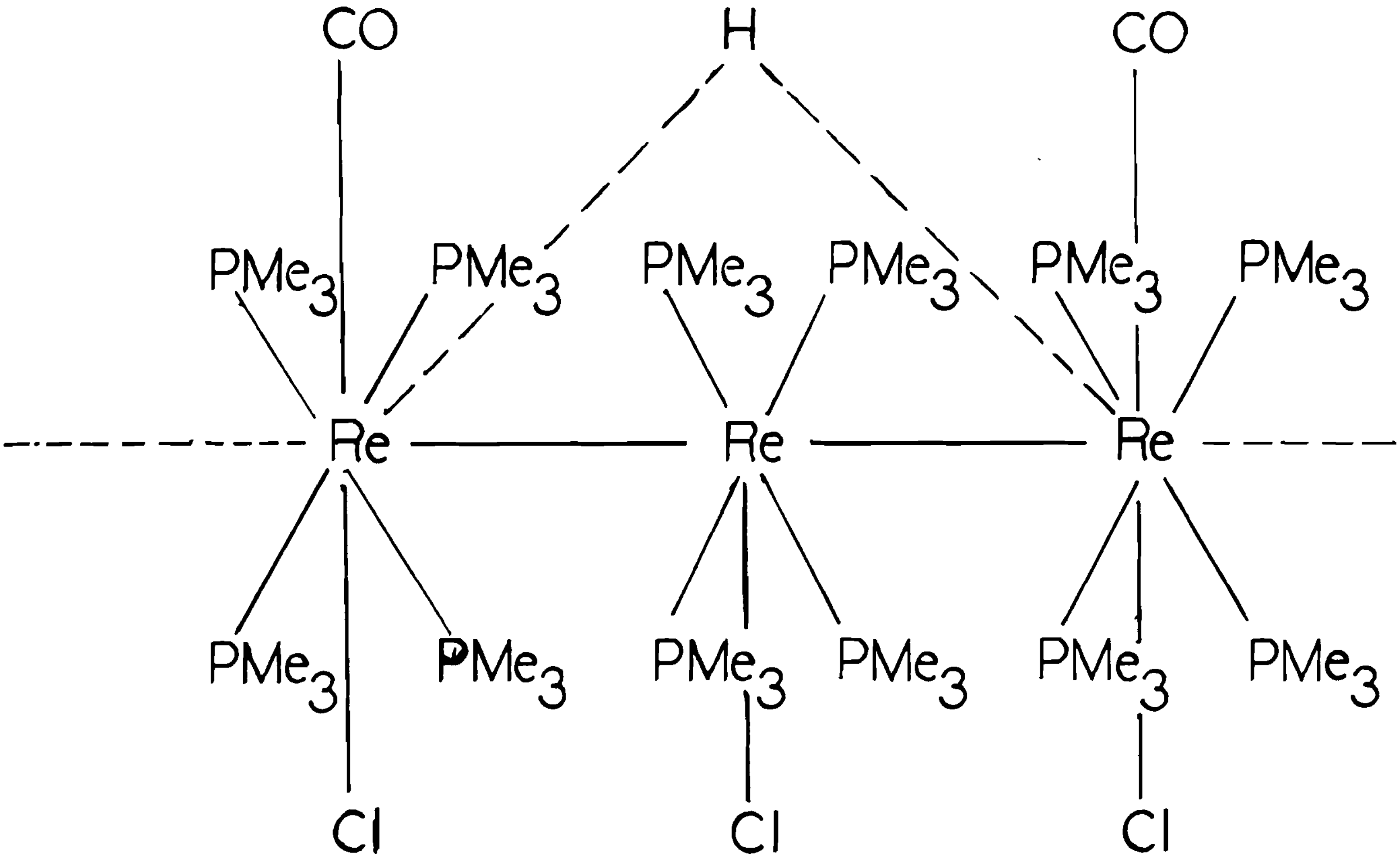

CO
H
CO
PMe3
PMe3
PMe3
PMe3
PMe3
PMe3
Re
Re
Re
PMe3
PMe3
PMe3
PMe3
PMe3
PMe3
Cl
Cl
Cl

Figure 17

Backbonding from a Filled Metal d-Orbital to an Empty Phosphorus d-Orbital in the PR_3 Ligand

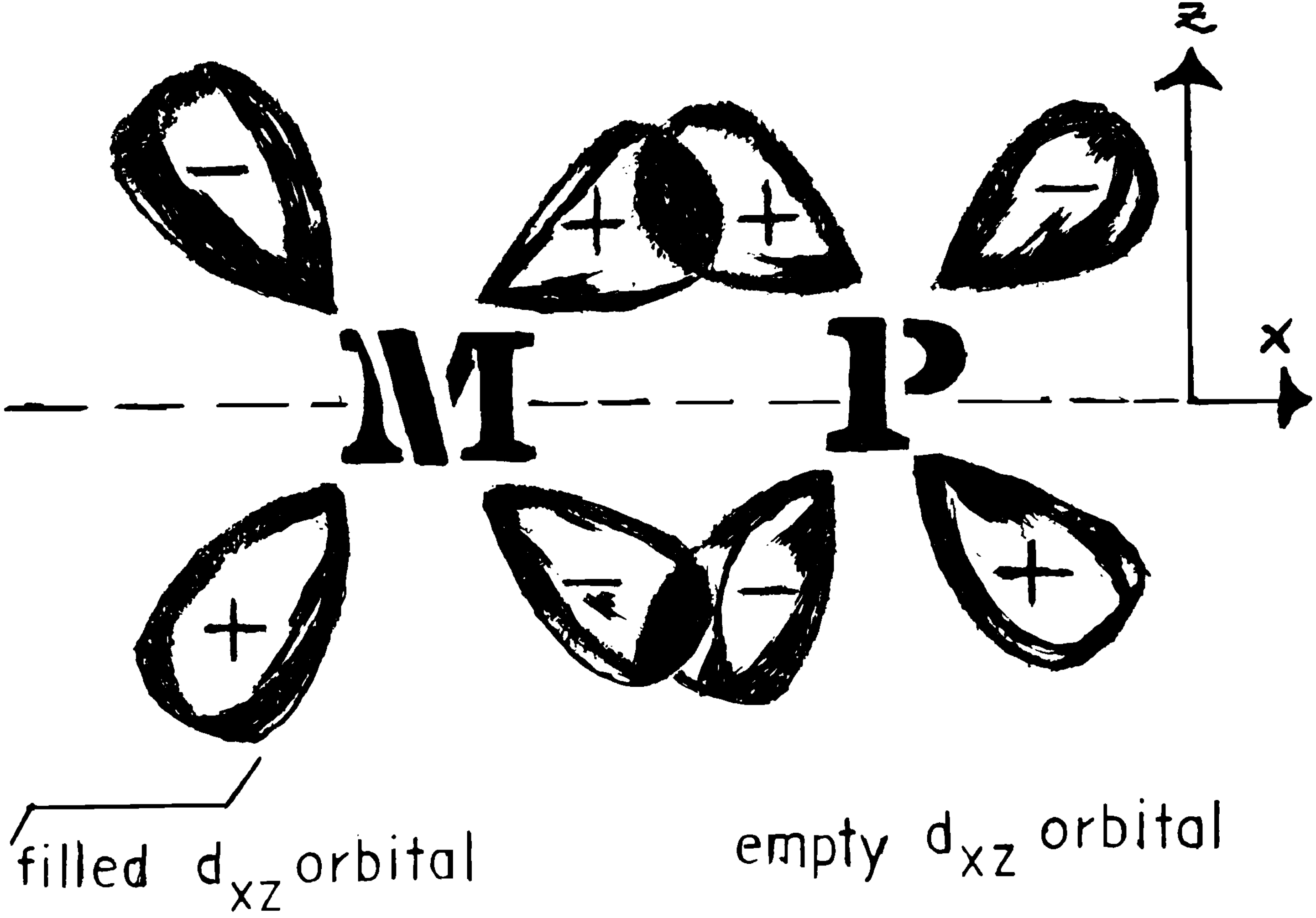
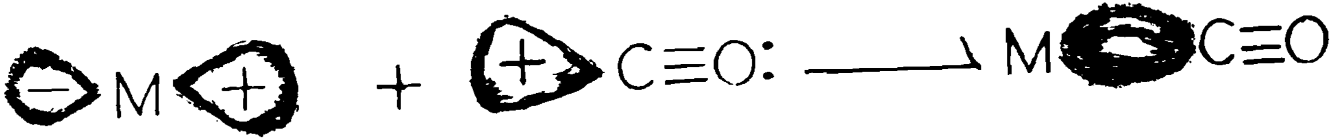

z
x
M
P
−
+
+
+
−
−
−
−
+
+
filled d_{xz} orbital
empty d_{xz} orbital

Figure 18

Sigma and Pi Metal-CO Interactions

σ– type



π– type

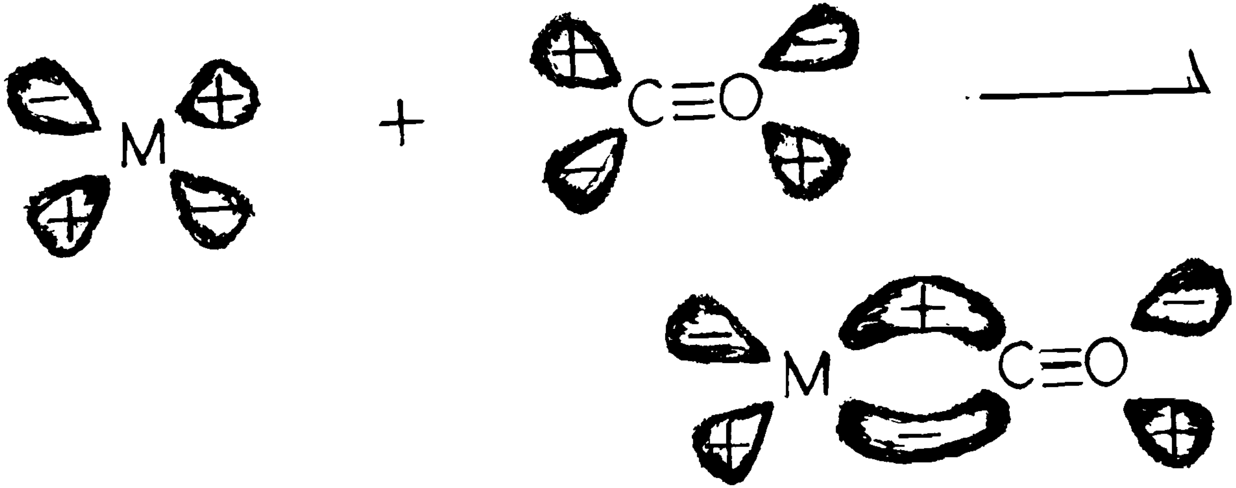


Figure 19

Possible Mixtures of Complexes as a
Result of Carbonylation
Reactions Between
CO and
$Re_2Cl_6(PPh_3)_2$

1. $ReCl_2(CO)_2(PPh_3)_2$
2. $ReCl(CO)_3(PPh_3)_2$
3. $Re_2Cl_5(PPh_3)_3$
4. $Re_3Cl_6(PPh_3)_2$
5. trans- $ReCl_4(PPh_3)_2$
6. $ReCl(CO)_2(PPh_3)_3$
7. $ReCl(CO)(PPh_3)_4$
8. $ReCl_3(CO)(PPh_3)_2$

Figure 20

Symmetry Elements of cis-$ML_4(CO)_2$,
C_{2v} Structure

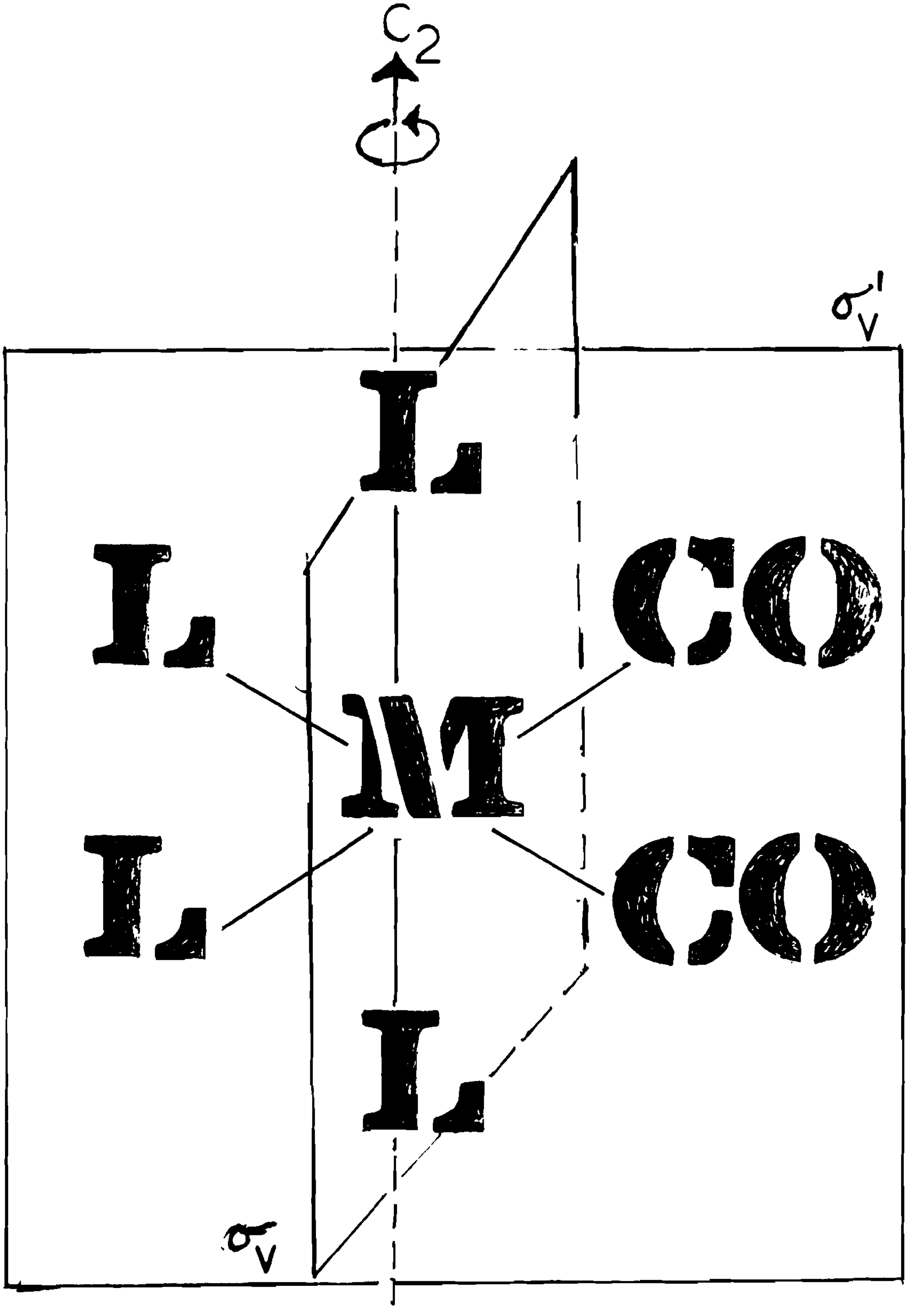

C2
σv'
L
L
CO
M
L
CO
L
σv

Figure 21

Symmetry Elements of trans-$ML_4(CO)_2$,
$\underline{D}_{4h}$ Structure

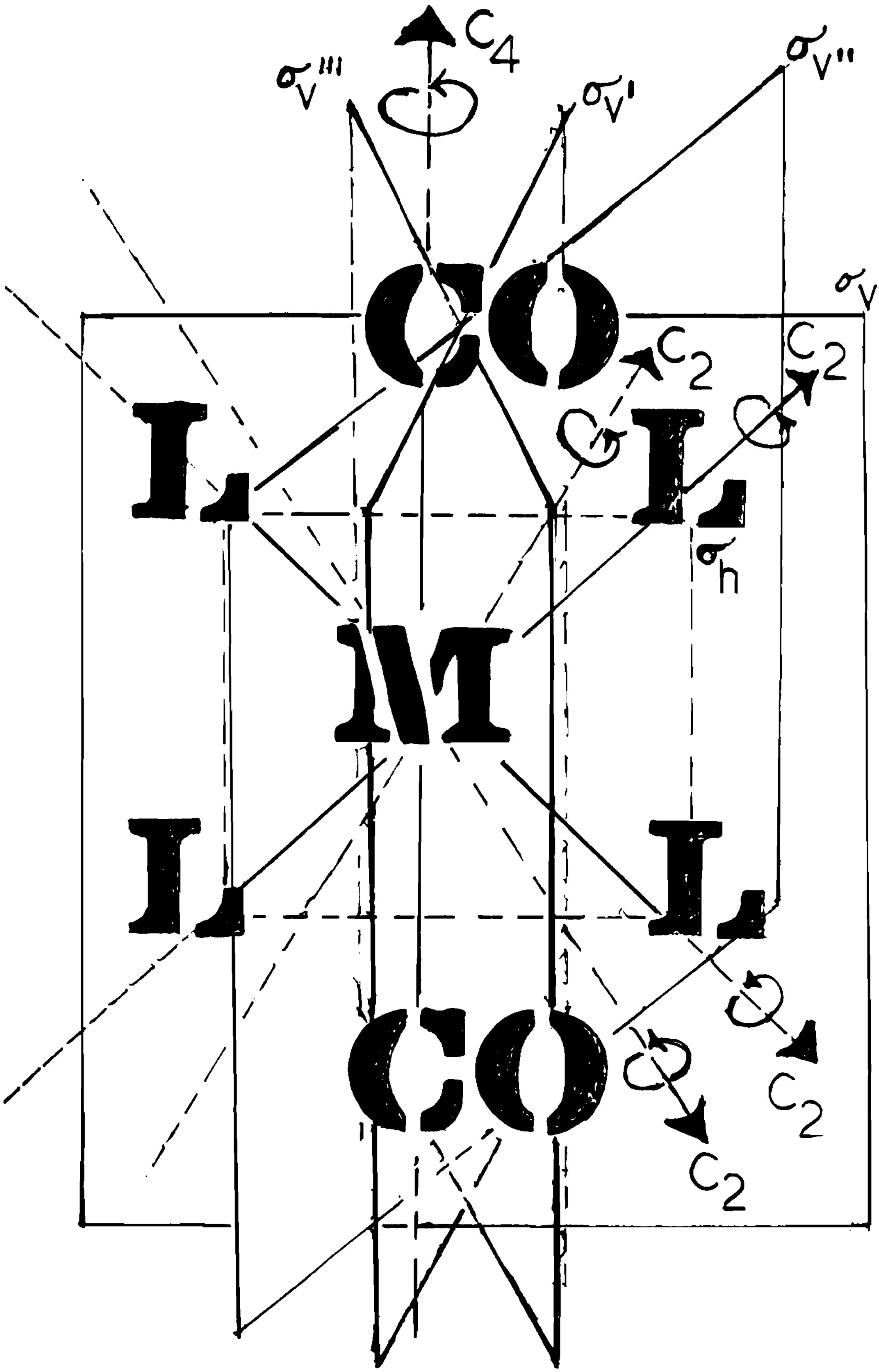

C4
σv'''
σv'
σv''
σv
CO
C2
C2
L
L
σh
M
L
L
CO
C2
C2

Figure 22

Heating Curve for a 0.00399 m Solution of $ReCl_2(CO)_2(PPh_3)_2$ in Benzene Solvent

Temperature (°C) vs. Time (min)

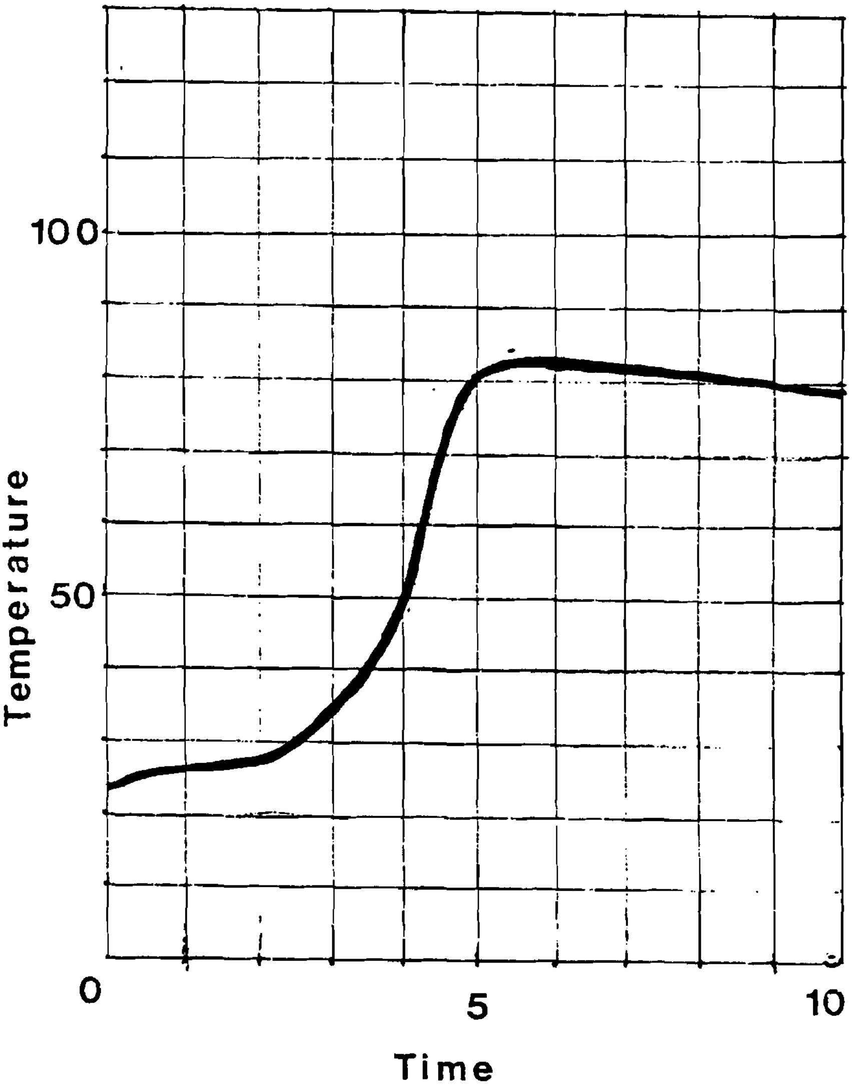
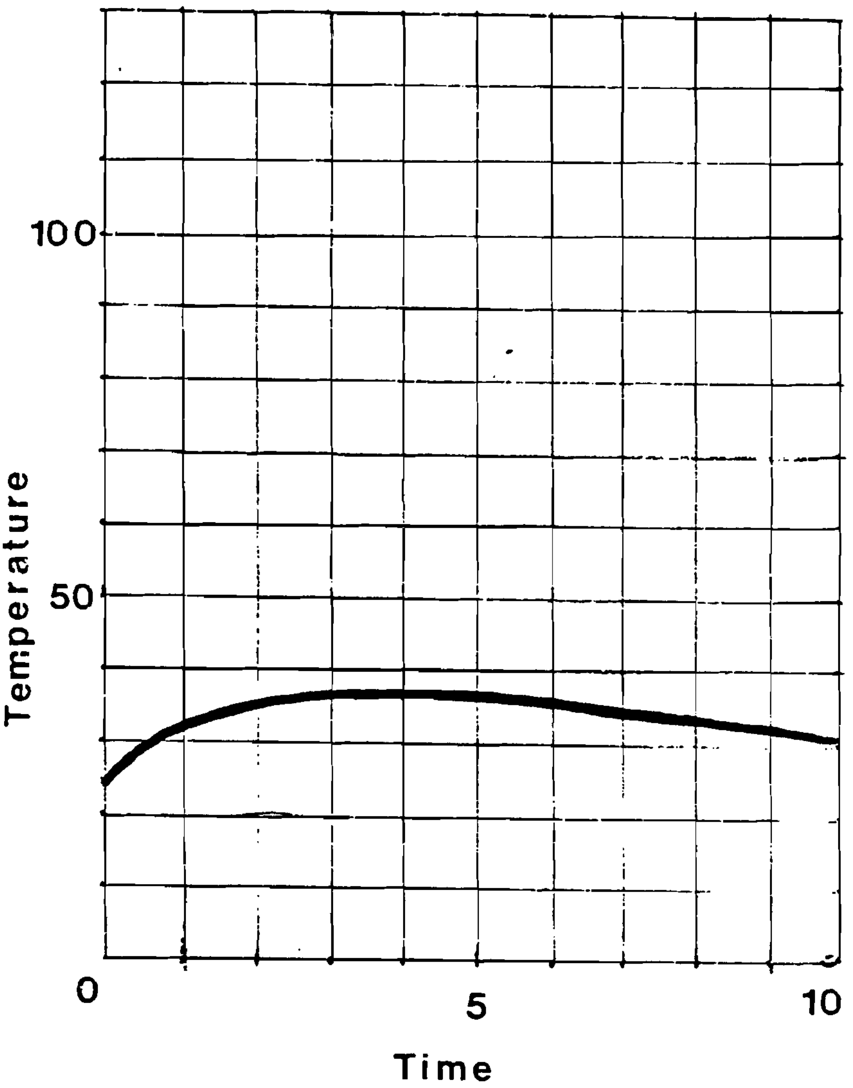

100
50
Temperature
0
5
10
Time

Figure 23

Heating Curve for Pure Diethyl Ether Solvent
Temperature (°C) vs. Time (min)



100
50
Temperature
0
5
10
Time

Figure 24

Heating Curve for a 0.0381 m Solution of Trimethylphosphine in Diethyl Ether Solvent

Temperature (°C) vs. Time (min)

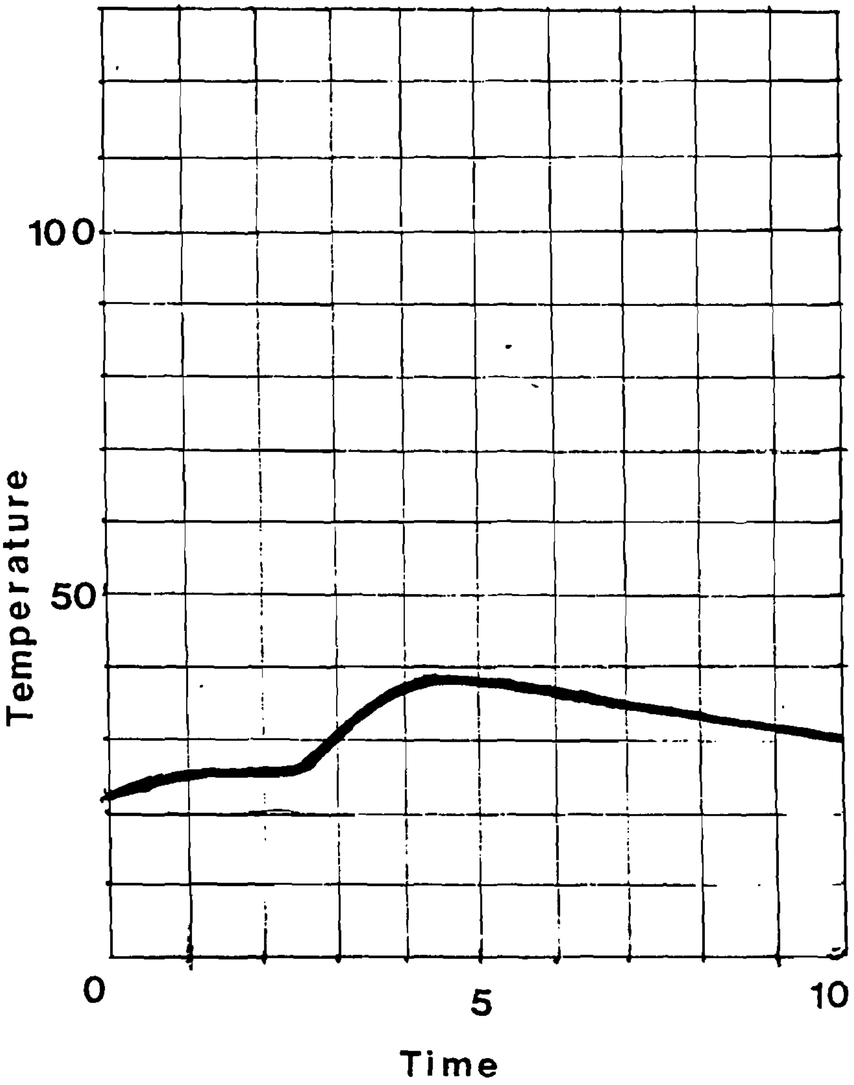

100
50
Temperature
0
5
10
Time

Figure 25

Heating Curve for Pure Methylene Chloride Solvent

Temperature (°C) vs. Time (min)

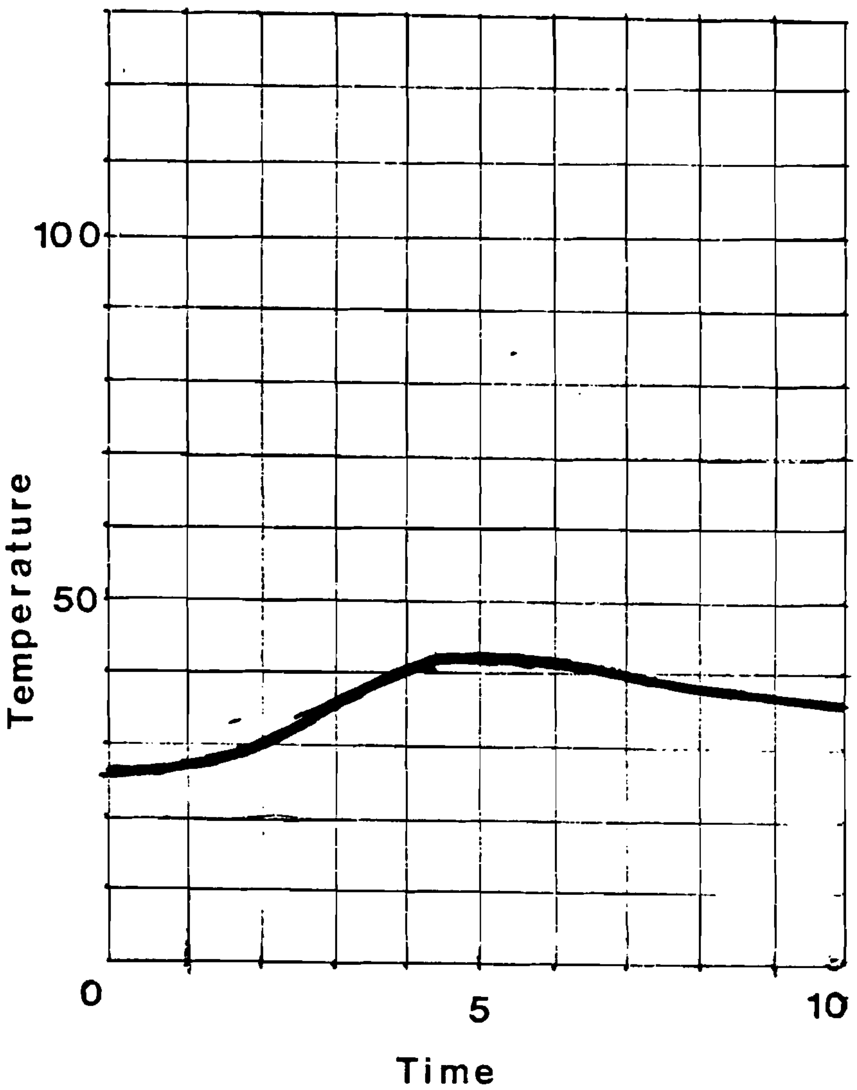
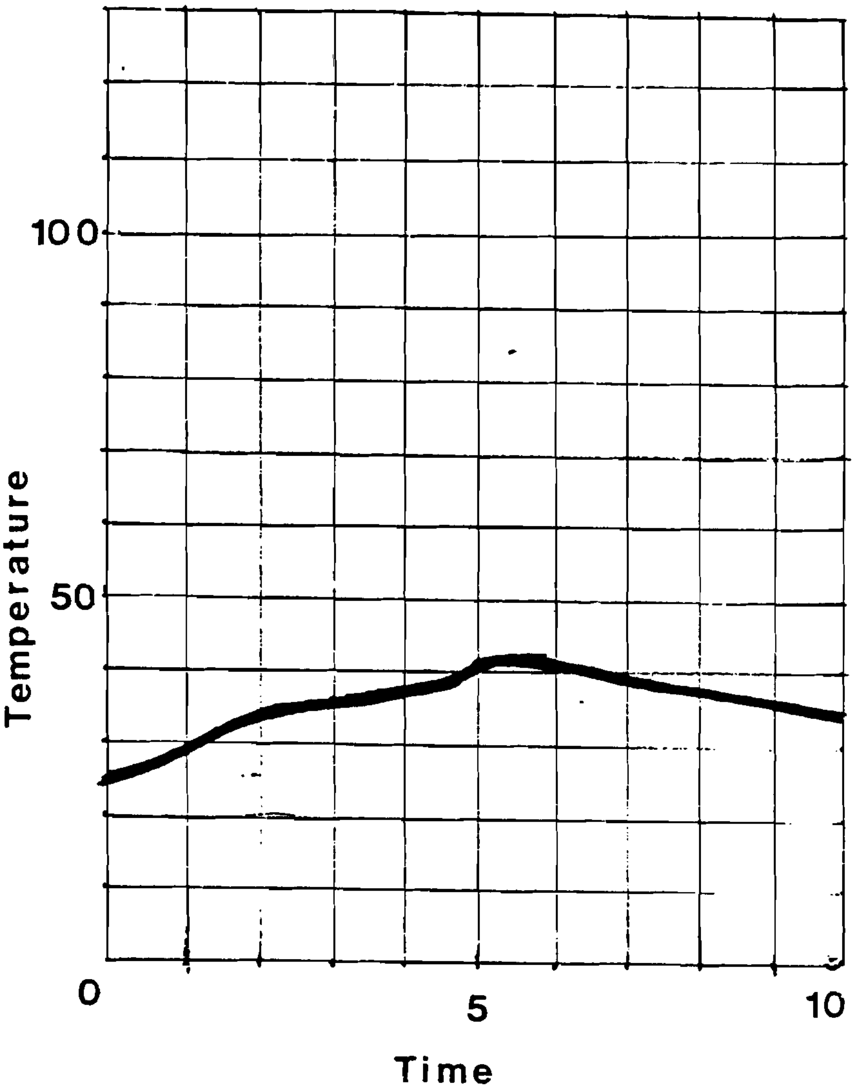

100
50
Temperature
0
5
10
Time

Figure 26

Heating Curve for a 0.00275 m Solution of $ReCl(CO)(PMe_3)_4$ in Methylene Chloride Solvent

Temperature (°C) vs. Time (min)


100
50
Temperature
0
5
10
Time

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Signature of Author

July 2, 1991
Date

PREPARATION AND CHARACTERIZATION OF CARBONYLTETRAKIS(TRIMETHYLPHOSPHINE)-RHENIUM(I) CHLORIDE
Title of Thesis

Jackie Tolbert
Signature of Graduate Office Staff Member

July 2, 1991
Date Received