ORGANOMETALLIC CHEMISTRY OF RHENIUM

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CONTENTS

ABBREVIATIONS

acac = acetylacetone
Bz = benzyl
bipy = bipyridyl
Cp = cyclopentadienyl

diars = 1,2-bis(diphenylarsino)ethane
diphos = 1,2-bis(diphenylphosphino)ethane
DME = dimethoxyethane
$f_n$fars = 1,2-bis(dimethylarsine)-*n*-fluoro-1-cyclobutene
$f_n$fos = 1,2-bis(dimethylphosphine)-*n*-fluoro-1-cyclobutene
o-phen = *o*-phenanthroline
THF = tetrahydrofuran
THT = tetrahydrothiophene
triars = 1,1,1-tris(dimethylarsinomethyl)ethane

I. INTRODUCTION

The large number of recent papers on organorhenium chemistry indicate an area of great research activity. This article is designed to survey the synthetic and structural chemistry of organorhenium compounds with emphasis on recent development.

A review[1] covering the inorganic chemistry of rhenium has appeared and two books[2,3] which briefly discuss organorhenium chemistry are available. In addition, there are several excellent reviews on the organometallic chemistry of transition metals which include organorhenium compounds[4-8]. In light of these reviews the kinetics and mechanisms of substitution reactions along with fluorocarbon derivatives will not be discussed.

Most organorhenium complexes are derived from dirhenium decacarbonyl, the halocarbonyls, or the hexacarbonylrhenium(I) cation. Hieber and Fuchs[9] first prepared dirhenium decacarbonyl by the high temperature reduction of Re_2O_7 with carbon monoxide under pressure.

$$Re_2O_7 + 17CO \rightarrow Re_2(CO)_{10} + 7CO_2$$

Quantitative yields were reported after 16 h with an initial CO pressure of 200 atm at 250°. Good results were obtained using ReO_3, ReO_2, and Re_2S_7, but $KReO_4$ gave poor yields. Attempts to dehalogenate rhenium pentacarbonyl halides with silver or copper under high CO pressure were unsuccessful as were attempts to synthesize the compound directly from finely divided rhenium metal[10].

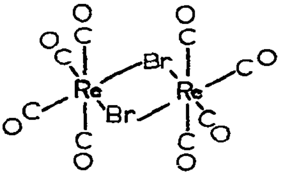
In another high pressure synthesis, $Re_2(CO)_{10}$ was prepared from anhydrous $ReCl_3$ or $ReCl_5$ using sodium in THF as the reducing agent[11]. A yield of 70% was obtained by operating at 130° and 250 atm of carbon monoxide for eight hours. Such a tedious workup procedure is involved that this method does not offer any advantages over the reactions using Re_2O_7.

Recently, Russian workers[12] have reported that dissolving Re_2O_7 in an organic solvent allows decreasing the carbon monoxide pressure to 120–140 atm at 200°. Good yields of $Re_2(CO)_{10}$ were reported after 12–15 h, but the authors failed to specify which organic solvent was used.

An X-ray diffraction study[13] has shown that the rhenium atoms in $Re_2(CO)_{10}$ are linked by a metal–metal bond with each metal octahedrally coordinated to five carbonyl ligands. The joined octahedra are rotated 45° with respect to each other to give a molecule with D_{4d} symmetry. The Re–Re distance is approximately 3.02 Å.

The three halide derivatives $R(CO)_5X$ (X = Cl, Br, I) were originally prepared by the carbonylation of $ReCl_5$, $ReCl_3$ or K_2ReX_6 at 200–230° and 200 atm in the presence of copper as halogen acceptor[14]. These compounds were also prepared by the carbonylation of rhenium metal in the presence of anhydrous metal halides or from the reaction of $KReO_4$ with organic halides[10]. In an attempt to prepare $Re_2(CO)_{10}$, rhenium pentachloride and iron pentacarbonyl were subjected to high temperature and pressure in an autoclave[15], but instead of the desired $Re_2(CO)_{10}$, $Re(CO)_5Cl$ was obtained in 30% yield.

If $Re_2(CO)_{10}$ is available, the compounds can be prepared at room temperature and pressure. Cleavage of the metal–metal bond in $Re_2(CO)_{10}$ by either chlorine or bromine in an inert solvent leads to the appropriate rhenium pentacarbonyl halide[16]. The iodine compound is more conveniently prepared by irradiation of $Re_2(CO)_{10}$ and iodine with UV light at room temperature[17]. Heating the monomeric derivatives $Re(CO)_5X$ to about 100° removes one mole of carbon monoxide, giving the tetracarbonyl dimers $[Re(CO)_4X]_2$ [18]. Structure (I) has been suggested for the dimers on the basis of their infrared spectra in the ν(CO) region. A single-crystal X-ray diffraction study[19] of the analogous manganese complex, $Mn_2(CO)_8Br_2$, has shown it to have this structure.



I

The hexacarbonylrhenium(I) cation has been prepared by the carbonylation of $Re(CO)_5Cl$ at high temperatures and pressures in the presence of anhydrous aluminum chloride[20]:

$$Re(CO)_5Cl + AlCl_3 + CO \xrightarrow[90^\circ]{320\text{ atm}} [Re(CO)_6][AlCl_4]$$

This stable cation could also be isolated as the reineckate, tetraphenylborate, perchlorate, tetracarbonylcobaltate(–I), $[Co(CO)_4]^-$, or nitrosyltricarbonylferrate(–I), $[Fe(CO)_3NO]^-$, salts. Anhydrous ferric chloride or zinc chloride, which yields $[Re(CO)_6]_2[Zn_2Cl_6]$, can also function as halide acceptors[21].

II. GROUP IVA DERIVATIVES OF RHENIUM CARBONYL

A. σ Bonded carbon derivatives

The pentacarbonyl rhenate anion $Re(CO)_5^-$ is a convenient precursor to many rhenium carbonyl derivatives. This anion is prepared by the reduction of $Re_2(CO)_{10}$ with a 1% sodium amalgam in THF solution[22] followed by reaction with an organic halide to yield compounds having the general formula $RRe(CO)_5$:

$$Re_2(CO)_{10} + 2Na(Hg) \rightarrow 2NaRe(CO)_5$$

$$NaRe(CO)_5 + RX \rightarrow RRe(CO)_5 + NaX$$

A list of the known alkyl, aryl and acyl derivatives of this type is summarized in Table 1. In general, the acyl derivatives can be converted to the corresponding alkyl and aryl compounds by heating.

A structural investigation[32] of $(p\text{-}ClC_6H_4CO)Re(CO)_5$, the only $RRe(CO)_5$ complex so far studied, indicates a rhenium–acyl carbon distance of 2.22 Å which is close to that expected for a single bond. This is surprising as infrared studies[33] of $MeCORe(CO)_5$ suggest the rhenium–acetyl linkage has a significant amount of double bond character. Further crystallographic studies on $RRe(CO)_5$ complexes are needed.

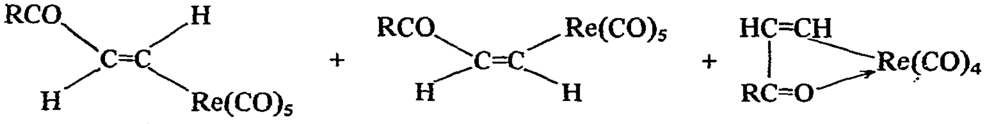
TABLE 1

ALKYL, ARYL AND ACYL DERIVATIVES WITH THE FORMULA $RRe(CO)_5$

R	Color	M.p. (°C)	Reference
CH_3	colorless	120	23
CH_3CO	pale yellow	80–81	24
C_6H_5CO	canary yellow	120 (dec.)	24
C_6H_5	colorless	46–47	24
$C_6H_5CH_2$	light yellow	33–34	24
$p\text{-}ClC_6H_4CO$	yellow	131–133	25
$p\text{-}BrC_6H_4CO$	yellow	129–131	25
$p\text{-}IC_6H_4CO$	light yellow	119–121	25
$o\text{-}ClC_5H_4CO$	yellow	95–97	26
$m\text{-}ClC_6H_4CO$	yellow	114–116	26
$p\text{-}ClC_6H_4$	white	81–82	25
$p\text{-}BrC_6H_4$	colorless	78–80	25
$p\text{-}IC_6H_4$	colorless	55–57	25
$o\text{-}ClC_6H_4$	colorless	65–67	26
$m\text{-}ClC_6H_4$	colorless	76–77	26
$o\text{-}CH_3C_6H_4CO$	yellow	73–74	27
$m\text{-}CH_3C_6H_4CO$	yellow	94–95	27
$p\text{-}CH_3C_6H_4CO$	yellow	120–122	27
$m\text{-}CH_3C_6H_4$	colorless	33–35	27
$p\text{-}CH_3C_6H_4$	colorless	53–55	27
CH_2CH_2CHCO	white	100–101	28
$cis\text{-}CH_3COCH{=}CH$	pale yellow	59–60	29
$trans\text{-}CH_3COCH{=}CH$	colorless	88–89	29
$cis\text{-}C_6H_5COCH{=}CH$	pale yellow	70	29
$trans\text{-}C_6H_5COCH{=}CH$	colorless	116–117	29
$C(C_6H_5)_3$	pale yellow	98–100	30
$1,2\text{-}CH_3B_{10}H_{10}CCO$		122–123	31
$1,2\text{-}C_6H_5CB_{10}H_{10}CCO$		131	31

The *cis* and *trans* isomers of the σ-complex $RCOCH{=}CHRe(CO)_5$ described in Table 1 result from the reaction of *trans*-2-chlorovinyl ketones with the rhenium pentacarbonyl anion[29]. In addition, the reaction mixture contains a compound in which the keto group is coordinated:

trans-$RCOCH{=}CHCl + NaRe(CO)_5 \rightarrow$



(R = Me, Ph)

The *trans* derivative is quite stable in air, but the *cis* derivative readily loses CO, even in the dark, to yield the keto coordinated compound.

Bis(rhenium pentacarbonyl) compounds[34] have been prepared from *para*- and *meta*-phthaloyl chloride:

$$2NaRe(CO)_5 + m,p\text{-}C_6H_4(COCl)_2 \rightarrow m,p\text{-}C_6H_4[CORe(CO)_5]_2 \xrightarrow{-2CO} m,p\text{-}C_6H_4[Re(CO)_5]_2$$

The *meta* isomer is converted to the phenylene derivative in solution at room temperature, but the *para* isomer must be refluxed in diglyme to remove the acyl carbonyl group.

Ethyl chloroformate combines with $NaRe(CO)_5$ to give the ester $Re(CO)_5CO_2Et$[35]:

$$NaRe(CO)_5 + ClCO_2Et \xrightarrow[\text{warm}]{\text{THF}} Re(CO)_5CO_2Et$$

Another route to ester derivatives is through the addition of alkoxides to $[Re(CO)_6]^+$ [36] or $[Re(CO)_4L_2]^+$ [37] ($L = PPh_3$, $\frac{1}{2}C_{12}H_8N_2$) where the nucleophile attacks a carbonyl carbon atom. The parent cationic compounds are readily regenerated by adding HCl to the ester derivatives:

$$Re(CO)_6^+ + OR^- \xrightarrow[0°]{\text{MeOH}} Re(CO)_5CO_2R$$

(R = Me, Et)

Chloroacetamide reacts with $NaRe(CO)_5$ to give the amide derivative which may be readily hydrolyzed to the corresponding acid $Re(CO)_5CH_2COOH$ [38].

B. Other Group IVA σ bonded derivatives

Group IVA elements form covalent bonds with rhenium by reaction of the appropriate halide compounds with the sodium salt of rhenium pentacarbonyl. These complexes will then undergo reactions with halogens, hydrohalic acids, and triphenyl derivatives of Group

$$R_{4-n}MX_n + n\text{NaRe(CO)}_5 \xrightarrow{\text{THF}} R_{4-n}M[\text{Re(CO)}_5]_n + n\text{NaX}$$

(R = organic group, M = Ge, Sn, Pb)

VA elements to yield a variety of substituted products. A list of these complexes and their derivatives is given in Table 2. The compound $Cl_2Sn[Re(CO)_5]_2$ can also be prepared by the insertion of anhydrous $SnCl_2$ into the rhenium–rhenium bond of $Re_2(CO)_{10}$ under ultraviolet irradiation[45]. One possible mechanism is homolytic cleavage of the Re–Re bond with formation of two pentacarbonyl radicals, $\cdot Re(CO)_5$, which then react with $SnCl_2$. Another view is one in which the Re–Re bond is not broken but is substantially weakened during UV irradiation and thus readily subject to the attack of $:SnCl_2$. Addition of ethanedithiol and triethylamine to this dichlorotin compound leads to a sulfur-containing heterocycle[42]. The amine is necessary to form the $[(C_2H_5)_3NH]^+$ cation before the reaction will proceed. Of additional interest is the formation of rhenium–tin compounds with an additional metal bonded to the tin atom[46,47]. Other details on the preparation of these compounds is lacking.

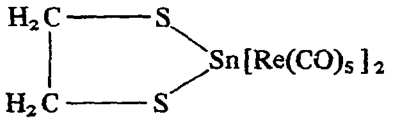
TABLE 2

GROUP IVA–RHENIUM CARBONYL COMPLEXES

M = Ge, Sn; R = CH_3, n-C_4H_9, CH=CH_2; X = Cl, Br; E = P, As, Sb

	Reference		Reference
$Ph_3MRe(CO)_5$	39, 40, 44	$Ph_3MRe(CO)_4EPH_3$	40
$Me_3SnRe(CO)_5$	44	$X_3MRe(CO)_5$	37, 38, 42
$Ph_3PbRe(CO)_5$	44	$H_3GeRe(CO)_5$	43
$Ph_2M[Re(CO)_5]_2$	39, 40, 42	$PhBr_2SnRe(CO)_5$	39
$Me_2Sn[Re(CO)_5]_2$	42	$Ph_2ClGeRe(CO)_5$	41
$PhSn[Re(CO)_5]_3$	41	$X_2Sn[Re(CO)_5]_2$	39, 42
$RSn[Re(CO)_5]_3$	42	$XSn[Re(CO)_5]_3$	39, 41, 42
$Sn_2[Re(CO)_5]_6$	41		

$$HSCH_2CH_2SH + Cl_2Sn[Re(CO)_5]_2 + 2(C_2H_5)_3N \rightarrow$$

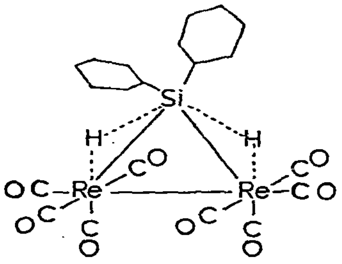


$+ 2[(C_2H_5)_3NH$

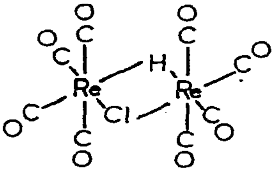
$$(CO)_5Mn\text{–}Sn(Ph)_2Cl + NaRe(CO)_5 \rightarrow (CO)_5Mn\text{–}Sn(Ph)_2Re(CO)_5$$

$$[CpFe(CO)_2]_2SnCl_2 + NaRe(CO)_5 \rightarrow [CpFe(CO)_2]_2Sn(Cl)Re(CO)_5$$

Compounds containing rhenium–silicon bonds have been prepared. Triphenylsilane[44] and trichlorosilane[48] react under vigorous conditions with $Re_2(CO)_{10}$ to give the products $Ph_3SiRe(CO)_5$ and $Cl_3SiRe(CO)_5$ respectively, while a compound with the stoichiometry $Ph_2SiH_2Re_2(CO)_8$ is prepared by ultraviolet irradiation of a benzene solution of $Re_2(CO)_{10}$ and Ph_2SiH_2 [49]. The molecular structure of the diphenylsilane complex[50] has been established by X-ray diffraction techniques and is shown by formula(II). While the hydrogen atoms were not located in the X-ray study, their existence is inferred from NMR, infrared, and mass spectral data. It has been reported[49] that this complex is readily converted to the dimeric hydride $[HRe(CO)_4]_2$, but preparative details are lacking.



II



III

The reaction of $NaRe(CO)_5$ with Ph_3SiCl in THF does not lead to a rhenium–silicon bond but instead gives a 95% yield of hexaphenyldisiloxane, $Ph_3SiOSiPh_3$, and a complex mixture of rhenium carbonyls[51]. The preparation of the disiloxane is interesting as the only source of oxygen is the carbonyl groups of the $[Re(CO)_5]^-$ anion. Acidification of the rhenium carbonyl mixture gives $HRe_3(CO)_{14}$ and the previously unreported $HRe_2(CO)_8Cl$. The latter compound is assigned structure (III) with bridging hydrogen and chlorine atoms on the basis of its fragmentation pattern, infrared spectrum, and the fact that (III) provides each rhenium with a rare gas configuration.

Cyclopentadienyl(trimethyl)stannane[52] and hexamethylditin[53] react with $Re_2(CO)_{10}$ by oxidative cleavage of the Re–Re bond. These reactions can be considered

$$CpSn(CH_3)_3 + Re_2(CO)_{10} \xrightarrow{220°} CpRe(CO)_3 + Me_3SnRe(CO)_5$$

$$Me_6Sn_2 + Re_2(CO)_{10} \xrightarrow[\text{triglyme}]{180°} 2Me_3SnRe(CO)_5$$

similar to the action of Br_2 on $Re_2(CO)_{10}$ to produce $Re(CO)_5Br$.

C. Insertion reactions

The reaction of $RRe(CO)_5$ ($R = Me, CH_2C_6H_5$) with refluxing sulfur dioxide gives the white, stable sulfinatopentacarbonyl complexes $Re(CO)_5SO_2R$ [54]. These compounds are assigned structures containing Re–S(O)$_2$–R linkages from their infrared and NMR spectral data. When R is the 2-alkenyl ligand, allylic rearrangement accompanies the insertion[55] to give the derivative $Re(CO)_5SO_2C(CH_3)_2CH{=}CH_2$. With sulfur trioxide, the hereto unknown sulfonato complexes $RSO_3Re(CO)_5$ (R = Me, Ph, *p*-$CH_3C_6H_4$) are produced[56]. The mechanisms of the SO_2 and SO_3 insertion reactions are not known.

$$RRe(CO)_5 + SO_3 \xrightarrow[CCl_4]{0^\circ} RSO_3Re(CO)_5$$

Carbon disulfide will insert into the rhenium–carbon σ-bond of $RRe(CO)_5$ at temperatures of 90–150° in a sealed tube, to give dithiocarboxylate complexes. A list of known derivatives is given in Table 3.

TABLE 3

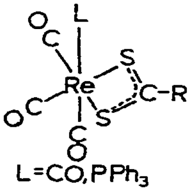
KNOWN COMPLEXES OF $RCS_2Re(CO)_4$

R	Reference
CH_3	57
C_6H_5	57
p-$CH_3C_6H_4$	58, 59
p-ClC_6H_4	58, 59
$C_6H_5CH_2$	59
$(C_6H_5)_3C$	59

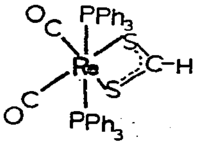
$$RRe(CO)_5 + CS_2 \rightarrow RCSSRe(CO)_4 + CO$$

The proposed structure (IV) of the dithiocarboxylate complexes has been confirmed by an X-ray diffraction study of the phenyl compound, $PhCS_2Re(CO)_4$ [60]. This compound reacts with triphenylphosphine in refluxing benzene liberating one mole of carbon monoxide and giving *cis*-$PhCS_2Re(CO)_3P(C_6H_5)_3$.

Carbon disulfide adds to hydridotris(triphenylphosphine)rheniumdicarbonyl[61] leading to the formation of (dithioformato)bis(triphenylphosphine)rheniumdicarbonyl which has structure (V). The hydride ligand of the parent compound is thought to have been transferred to the carbon atom of the entering CS_2 molecule although the hydrogen atom was not actually located by the X-ray diffraction study.



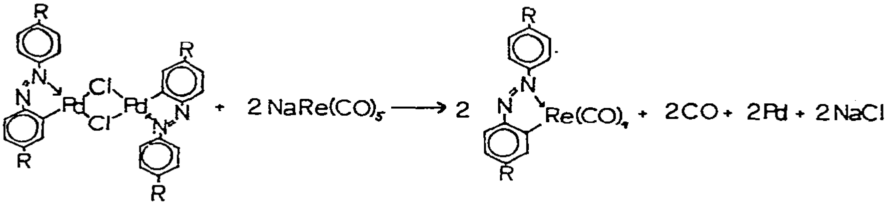
IV



V

D. Azobenzene derivatives

Heck[62] prepared the first rhenium carbonyl derivatives of azobenzene by a ligand exchange reaction of the rhenium pentacarbonyl anion with chloro-2-(phenylazo)phenylpalladium dimers. The compounds were obtained in low yields but are thermally quite stable. Later it was found that azobenzene will react directly with either $Re_2(CO)_{10}$ or $MeRe(CO)_5$ in refluxing petroleum ether (b.p. 100–120°) to give tetracarbonyl-2-(phenylazo)phenylrhenium[63]. Starting with $MeRe(CO)_5$ an 80% yield was obtained.



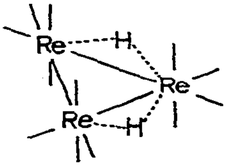
E. $HRe(CO)_5$

The hydrido derivative, $HRe(CO)_5$, has been prepared by the reaction of either phosphoric acid or water on the $Re(CO)_5^-$ anion[64,65]. The compound is a colorless, air-sensitive, very weakly acidic liquid which melts at 12°.

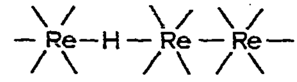
III. RHENIUM POLYNUCLEAR CARBONYLS

The reduction of $Re_2(CO)_{10}$, with sodium amalgam at room temperature in tetrahydrofuran, yields the pale yellow salt $NaRe(CO)_5 \cdot \frac{1}{2}C_4H_8O$. At reflux temperature, or on addition of $NaBH_4$, carbon monoxide is evolved and the solution acquires an intense red coloration. After acid hydrolysis, $HRe(CO)_5$, $Re_2(CO)_{10}$, and the polynuclear hydrides $H_3Re(CO)_{12}$ [66] and $HRe_3(CO)_{14}$ [67] are isolated in varing amounts although $H_3Re_3(CO)_{12}$ is more conveniently prepared by passing hydrogen through a decalin solution of $Re_2(CO)_{10}$ at 120°.[68].

Attempts to perform a detailed crystallographic analysis on $H_3Re_3(CO)_{12}$ have been unsuccessful. However, treatment of $H_3Re_3(CO)_{12}$ with base yields the anion $[H_2Re_3(CO)_{12}]^-$, isolated as the tetraphenylarsonium salt, for which an X-ray diffraction study has been published[69]. The anion has C_{2v} symmetry with the three rhenium atoms defining an approximate isosceles triangle (VI). While the hydrogen atoms were not detected in the crystallographic investigation, the proton NMR spectrum shows a sharp singlet at τ 27.2 characteristic for hydrogen bonded to rhenium. This information, along with consideration of the Re–Re distances, indicates the hydrogen atoms are present somewhere along two sides of the triangle.



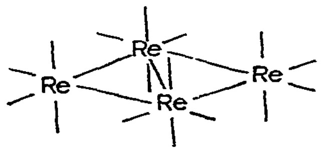
VI



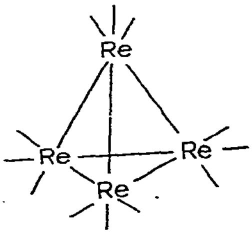
VII

Likewise, a structural investigation of $HRe_3(CO)_{14}$ has not been reported. From NMR and infrared evidence the compound is thought to have the linear structure shown by formula (VII), at least in solution[67]. $HRe_3(CO)_{14}$ will react with carbon monoxide at atmospheric pressure to yield $HRe(CO)_5$ and $Re_2(CO)_{10}$ [70].

Evaporation to dryness of the red colored solution described previously, followed by dissolving the residue in acetone and addition of tetra-n-butylammonium iodide[71,72], gives a compound of stoichiometry $[(n\text{-}C_4H_9)_4N]_2[Re_4(CO)_{16}]$. The stereochemistry of the anion (VIII) shows that the four rhenium atoms lie in a plane.



VIII



IX

An ion of stoichiometry $[H_6Re_4(CO)_{12}]^{2-}$ has been prepared[73] by refluxing a THF solution of $Re_2(CO)_{10}$ and $NaBH_4$ overnight, followed by stirring at room temperature for several days. This dianion is then isolated as the tetraphenylarsonium salt. The four rhenium atoms define a tetrahedron (IX) with three carbonyl groups attached to each metal ion. Although the six hydride ligands were not detected in the crystallographic analysis, the proton NMR shows a single peak at τ27.4 indicating the hydrogens are equivalent. In all probability, a hydrogen atom lies along each edge of the tetrahedron bridging two rhenium atoms.

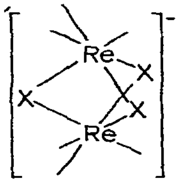
A compound with the formula $H_4Re_4(CO)_{12}$ is produced[74] by heating $H_3Re_3(CO)_{12}$ in decalin at 190° for 30 min or is prepared by passing hydrogen through a decalin solution of $Re_2(CO)_{10}$ at 170^{c} [68]. Infrared and NMR evidence suggest the four rhenium atoms form a tetrahedral cluster which must be unsaturated if each metal is to attain an inert gas configuration. The compound may be considered as being derived from the $[H_6Re_4(CO)_{12}]^{2-}$ ion by losing two hydride ions.

The rhenium hydride ion $[ReH_9]^{2-}$ has been found to react with a stream of carbon monoxide in the following manner[75]:

$$[(C_2H_5)_4N]_2ReH_9 + CO \xrightarrow{\text{alc. } OH^-} [(C_2H_5)_4N]Re_2(CO)_6X_3$$

$(X = H, EtO, i\text{-}PrO)$

NMR and infrared evidence suggest a structure (X) where two $Re(CO)_3$ moieties are bridged by three X groups. For the hydride complex, a single resonance at τ27.49 is found demonstrating the presence of rhenium bonded hydrogen. This value is considerably higher than what has been found for non-bridging rhenium bonded hydrogen, (e.g., τ15.7 for $HRe(CO)_5$[11] and τ18.5 for $[ReH_9]^{2-}$ [76]), but is in good agreement with the τ26.25 value reported[67] for the bridging hydrogen in $HRe_3(CO)_{14}$ and the τ27.4 value reported[73] for the bridging hydrogens in the $[H_6Re_4(CO)_{12}]^{2-}$ anion.



$(X = H^-, EtO^-, i\text{-}PrO^-)$

X

Finely divided rhenium heptasulphide, intimately mixed with copper powder, has been carbonylated to yield a mixture of $Re_2(CO)_{10}$ and the polynuclear tetracarbonyl $[Re(CO)_4]_x$ [77]:

$$Re_2S_7 + Cu + CO \xrightarrow[85 \text{ atm}]{200^\circ/7 \text{ h}} Re_2(CO)_{10} + [Re(CO)_4]_x$$

The insolubility of the tetracarbonyl complex prevented a determination of its molecular weight. The simplest structure which would allow each rhenium to obtain an inert gas configuration is a tetramer in which the rhenium atoms are located at the corners of a tetrahedron.

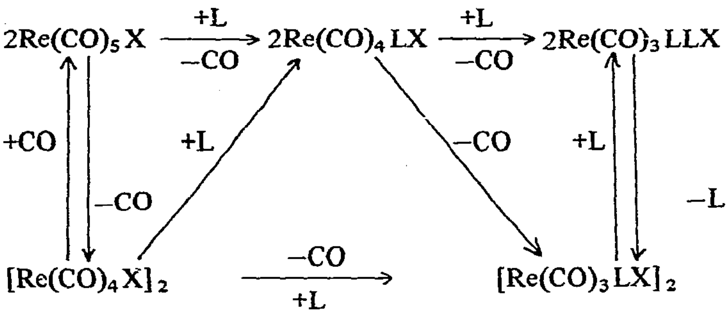
IV. SUBSTITUTION REACTIONS OF RHENIUM CARBONYL COMPLEXES

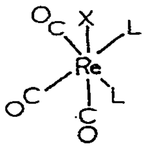
Dirhenium decacarbonyl, the rhenium carbonyl halides and hexacarbonylrhenium(I) cation undergo reactions with a wide variety of ligands. These ligands replace carbonyl or other groups in the complexes, and in addition, products may be isolated which indicate nucleophilic attack on a carbonyl carbon. Substituted carbonyl complexes also result from the carbonylation of rhenium complexes. Few crystal structures are reported for these substituted rhenium carbonyl complexes and most structures have been assigned from IR, NMR and dipole moment studies.

A. Rhenium carbonyl halides and hexacarbonylrhenium (I) cation

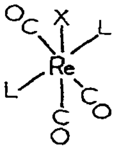
The CO groups in $[Re(CO)_6]^+$ are more inert to substitution than those of the rhenium carbonyl halides[7,78]. The dissociative lability of the CO groups in $Re(CO)_5X$ depends on the nature of X with I, Br, Cl, NCO and H groups labilizing the CO groups as compared to $[Re(CO)_6]^+$ [7].

Substitution of CO groups in $Re(CO)_5X$ and $[Re(CO)_4X]_2$ (X = Cl, Br, I) occurs readily in organic solvents and may be represented by Scheme 1. Monosubstituted complexes $Re(CO)_4LX$ are most readily isolated from the reaction of $[Re(CO)_4X]_2$ with a stoichiometric amount of the ligand under mild conditions[79]. With excess ligand the tricarbonyl complexes $Re(CO)_3L_2X$ are usually obtained from either $Re(CO)_5X$ or $Re_2(CO)_8X_2$. These tricarbonyl complexes have three structural possibilities (XI), (XII), and (XIII). Substituted tricarbonyl complexes are observed with structure (XI) *fac*, and (XII) *mer*, with steric requirements favoring the *mer* arrangement but *trans* effects favoring the *fac* arrangement[78].

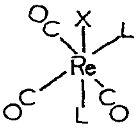




XI



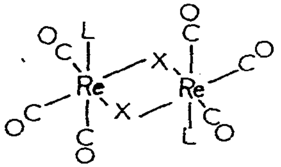
XII



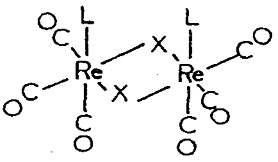
XIII

The halogen bridged complexes $Re_2(CO)_6L_2X_2$ are assigned structures (XIV) and (XV) in which the substitution is *cis* to the halogen bridge. Three ν(CO) bands are predicted for (XIV) and five for (XV). If coupling between the two halves of the molecule is negligible, however, three bands would also be predicted for (XV).

Further substitution to yield mono- and dicarbonyl complexes takes place only under more rigorous reaction conditions, such as evacuated sealed tube reactions[80].



XIV



XV

1. *Isonitrile and nitrile complexes*

Few isonitrile derivatives of rhenium(I) have been reported. *p*-Tolylisonitrile reacts with $Re(CO)_5Cl$ to yield a cationic tetracarbonyl[81]:

$$Re(CO)_5Cl + RNC \xrightarrow[100^\circ]{\text{Petr. ether}} [Re(CO)_4(RNC)_2]Cl$$

The complex reacts with pyridine to eliminate carbon monoxide and isonitrile to yield $Re(CO)_3(C_5H_5N)_2X$. It is surprising that an ionic derivative is formed in light of the nonionic, phenylisocyanide derivatives of manganese(I) $Mn(CO)_x(RNC)_{5-x}Br$ [82]. The mixed phosphine–isonitrile complexes $[Re(CO)(PPh_3)_2(RNC)X]_x$, and $Re(CO)(PPh_3)_2(RNC)_2Cl$ (R = *p*-MePh, X = Cl, Br) have also been reported[83].

Organonitriles react with rhenium(I) halocarbonyls to give either mononuclear or binuclear complexes.

$[Re(CO)_4Br]_2 + 2CH_3CN \rightarrow 2Re(CO)_4(CH_3CN)Br$ [84]
$Re(CO)_5X + 2RCN \rightarrow Re(CO)_3(RCN)_2X + 2CO$
(X = Cl, Br; R = Me [85]) (X = Br; R = Me, Et, C_2H_3, Ph [84])
$2Re(CO)_5X + 2RCN \rightarrow Re_2(CO)_6(RCN)_2X_2$
(X = Cl, Br, I; R = Me [86])

Infrared evidence suggests that the nitriles are σ bonded to the metal. The IR spectra in the carbonyl stretching region are consistent with a *fac* arrangement (XI) for $Re(CO)_3(RCN)_2X$ and a *cis* structure for $Re(CO)_4(MeCN)Br$. The binuclear complexes are formulated as halogen bridged complexes of structure (XIV).

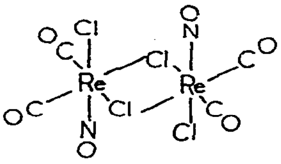
Reactions of malono-, succino-, and glutaronitrile with $Re(CO)_5X$ have been reported to yield monomeric complexes $Re(CO)_3$(dinitrile)X in which the nitriles are considered to be π bonded to the metal[85]. Additional studies, however, suggest that these complexes should be formulated as halogen bridged dimers with σ bonded nitriles[87]. The acetonitrile complex $[Re(CO)_5(MeCN)]^+$ has been reported from the reaction of $Re_2(CO)_{10}$ with $NOPF_6$ [88].

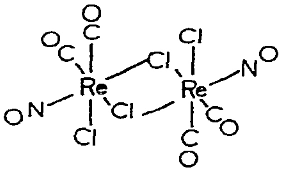
2. *Nitrosyl–carbonyl complexes*

Nitrosyl chloride or nitric oxide in the presence of hydrogen chloride reacts with $Re_2(CO)_8Cl_2$ in benzene to yield the chlorine bridged $Re_2(CO)_4(NO)_2Cl_4$ [89]:

$$Re_2(CO)_8Cl_2 + NOCl \rightarrow Re_2(CO)_4(NO)_2Cl_4$$

The bromo and iodo derivatives are obtained by metathesis with the corresponding potassium halides. The dimeric formulation is based on the appearance of the parent molecular ions in the mass spectra. Structures (XVI) and (XVII) are considered most probable on the basis of infrared and molecular weight data. The NO stretching vibration for the chloro complex appears at 1803 cm^{-1} which is consistent with a +1 oxidation state for the NO group.


XVI

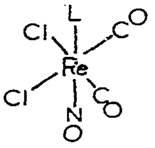

XVII

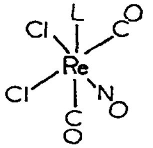
The halogen bridges in the nitrosyl complexes are readily cleaved by oxygen, sulfur, nitrogen and phosphorous donor ligands[89,90]. Pseudo first order kinetic experiments for

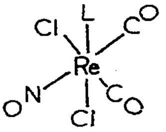
$$Re_2(CO)_4(NO)_2X_4 + 2\ L \rightarrow 2\ Re(CO)_2(NO)LX_4$$

($X = Cl$; $L = C_5H_5N$ [89]; 2-F [90], 2- or 3-Cl [90], 3- or 4-CN [90], 4-CH_3 [89] or 3,4-$(CH_3)_2$ [89] pyridine; C_5H_5NO [89]; Ph_3PO [89]; C_4H_8S [89]).
($X = Br, I$; $L = C_5H_5N$ [89]).

the cleavage of the chloride bridges in $Re_2(CO)_4(NO)_2Cl_4$ by chloro-, fluoro-, and cyano-pyridines indicate that the reactions are first order in both ligand and complex concentrations[90]. The probable structures for $Re(CO)_2(NO)(L)X_2$ which are in agreement with the infrared and molecular weight data are (XVIII), (XIX) and (XX) [89].


XVIII


XIX


XX

The complexes $Re_2(CO)_4(NO)_2Cl_4$ also react with β-diketones to yield stable, sublimable complexes[91].

$$Re_2(CO)_4(NO)_2Cl_4 + 2AH \rightarrow 2Re(CO)_2(NO)ACl + 2HCl$$

(AH = acacH, F_6acacH, Bz_2CH_2)

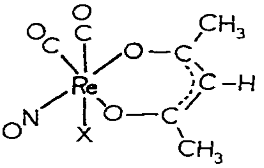
Structure (XXI) has been assigned to the acetylacetone derivative on the basis of its NMR and IR spectra.

The π donor ligand cyclooctene reacts with $Re_2(CO)_4(NO)_2Cl_4$ to yield a novel olefin complex[91]. Solution molecular weight studies in chloroform and IR studies suggest structure

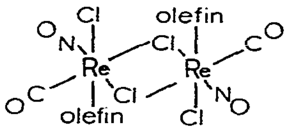
(XXII). No IR or NMR data for the complexed olefin are reported.

$$Re_2(CO)_4(NO)_2Cl_4 + 2\,C_8H_{14} \rightarrow Re_2(CO)_2(NO)_2(C_8H_{14})_2Cl_4 + 2CO$$

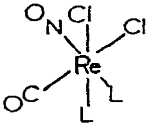
The complex (XXII) undergoes bridge splitting reactions with pyridine, 2-chloropyridine, triphenylphosphite and triphenylarsine to yield complexes of the stoichiometry $Re(CO)(NO)L_2Cl_2$ which may have structure (XXIII) [91].



XXI



XXII



XXIII

3. Ammonia and amine complexes

Ammonia reacts with chloropentacarbonylrhenium(I) to yield a diamagnetic carbamoyl complex[92,93]. Primary and secondary amines also yield carbamoyl complexes when allowed to react with Re^I complexes.

$$Re(CO)_5Cl + NH_3 \xrightarrow[1\ h]{60^\circ} Re(CO)_4(NH_3)CONH_2 + NH_4Cl$$

$$Re(CO)_5X + R_1R_2NH \rightarrow Re(CO)_4(R_1R_2NH)CONR_1R_2 + R_1R_2NH_2X$$

R_1 =	Me	i-Pr	n-Bu	C_6H_{11}	Me	C_5H_{10}	C_4H_8
R_2 =	H	H	H	H	Me	C_5H_{10}	C_4H_8
X =	Cl Br	Br	Br	Br	Cl Br	Br	Br
ref.	93 94	94	94	94	93 94	94	94

These carbamoyl complexes exhibit four ν(CO) bands which are consistent with a *cis* substitution pattern. The proposed structures are identical to that found for $Mn(CO)_4(NH_2CH_3)CONHCH_3$ [95].

The mechanism suggested for the formation of carbamoyl complexes involves a nucleophilic attack on a carbonyl carbon by the amine[93,94]. Whether the reaction proceeds through a $[Re(CO)_5(NH_2R)]^+$ or a $Re(CO)_4(CONH_3)X$ intermediate is still in question. Cationic intermediates may be favored because their carbonyl groups are susceptible to nucleophilic attack[93,96]. This mechanism is similar to that suggested for the reaction of the hexacarbonylrhenium(I) cation with alkoxides[36].

Further reaction of $Re(CO)_4(NH_3)CONH_2$ with ammonium chloride and ammonia yields the ionic products $[Re(CO)_4(NH_3)_2]^+$ and $[Re(CO)_3(NH_3)_3]^+$ [92,97]. The similar reaction with only ammonia is reported to yield $Re(CO)_3(NH_3)_2NCO$ and

$Re(CO)_3(NH_3)_2CN$ [92,93]. In addition both $HRe(CO)_5$ and $Re_2(CO)_{10}$ react with ammonia and ammonium chloride to yield $[Re(CO)_3(NH_3)_3]^+$ [97]. It is suggested that $HRe(CO)_5$ and $Re_2(CO)_{10}$ are oxidized by the ammonium chloride.

The carbamoyl complexes react with HCl to yield ionic pentacarbonyl complexes which can be isolated as hexafluorophosphate salts. The corresponding compound $[Re(CO)_5NH_3]^+$

$$Re(CO)_4(NRH_2)CONHR + 2HCl \rightarrow [Re(CO)_5(NH_2R)]^+Cl^- + RNH_3^+Cl$$

(R = H [94]; R = Me, $CH(CH_3)_2$ [94])

has also been isolated[97]. These ionic pentacarbonyl complexes are very susceptible to nucleophilic attack by amines, azide ion and iodide ion[94]. For example, the attack by isopropylamine results in a carbamoyl complex. The arrangement of the product suggests that the reaction proceeds by a direct attack on a carbonyl carbon and not by a NH_2CH_3 migration.

$$[Re(CO)_4NH_2CH_3]^+ + i\text{-}PrNH_2 \rightarrow Re(CO)_4(NH_2CH_3)CONHCH(CH_3)_2$$

If the nucleophile is azide ion or hydrazine, an isocyanate product $Re(CO)_4(NH_2CH_3)NCO$ results.

The carbonyl carbons in $[Re(CO)_6]^+$ are susceptible to nucleophilic attack by azide ion, hydrazine and isopropylamine[96]:

$$[Re(CO)_6]^+ + N_3^- \rightarrow Re(CO)_5NCO + N_2$$

$$[Re(CO)_6]^+ + 2N_2H_4 \rightarrow Re(CO)_5NCO + [N_2H_5]^+$$

$$[Re(CO)_6]^+ + 2(i\text{-}Pr)NH_2 \rightarrow Re(CO)_4[(i\text{-}Pr)NH_2]CON(i\text{-}Pr)H$$

In contrast, the reaction of $[Re(CO)_6]^+$ with ammonia is reported to yield $HRe(CO)_5$, NH_4^+ and urea[97]. The reaction of $[Re(CO)_6]^+$ with tetramethylethylenediamine is reported to yield $Re_2(CO)_{10}$ [79].

Isocyanato complexes have also been reported from the following reactions[98]:

$$Re(CO)_4LBr + N_2H_4 \rightarrow fac\text{-}Re(CO)_3L(N_2H_4)NCO$$

(L = $AsMe_2Ph$, PMe_2Ph, PPh_3)

$$mer\text{-}Re(CO)_3L_2X + N_2H_4 \rightarrow Re(CO)_2(N_2H_4)(L_2)NCO$$

(X = Cl, Br; L = PMe_2Ph, $PMePh_2$, PPh_3)

Both *cis*- and *trans*-$Re(CO)_4LBr$ yield identical products. However, only the *mer* isomer of $Re(CO)_3L_2X$ reacts with hydrazine. It is suggested that $Re(CO)_4LX$ and $Re(CO)_3L_2X$ dissociate into five coordinate cationic species which coordinate a hydrazine to yield a six-coordinate species which undergoes further reaction through a carbamoyl intermediate.

The coordinated hydrazine in $Re(CO)_3L(N_2H_4)NCO$ and $Re(CO)_2L_2(N_2H_4)NCO$ is readily replaced by phosphine ligands or carbon monoxide[98].

$Re(CO)_3(N_2H_4)L(NCO) + L \rightarrow mer\text{-}Re(CO)_3L_2NCO$
$(L = PMe_2Ph, PPh_3)$

$Re(CO)_2L_2(N_2H_4)(NCO) + CO \rightarrow mer\text{-}Re(CO)_3L_2NCO$

$Re(CO)_2L_2(N_2H_4)(NCO) + L \rightarrow Re(CO)_2L_3NCO$
$(L = PMe_2Ph, PMePh_2)$

Substituted tricarbonyl complexes of the stoichiometry $Re(CO)_3L_2NCO$ have also been isolated from the following reactions[96].

$Re(CO)_5NCO + L\text{–}L \rightarrow Re(CO)_3(L\text{–}L)NCO + 2CO$
(L–L = diphos, *o*-phen, 2,2′-dipy)

Infrared evidence suggests that these complexes have structure (XI). Kinetic studies indicate that the reaction obeys the first order rate law, rate = k_1 $[Re(CO)_5NCO]$ [96], which has also been obtained from similar studies with halopentacarbonylrhenium(I) complexes[7,99]. The value of k_1 at 60°C is significantly larger than the values for the halide complexes. The order of k_1 for the $Re(CO)_5X$ complexes is $NCO > Cl > Br > I$. This order is in agreement with the observation that a nitrogen donor ligand labilizes one or more of the remaining CO groups[7].

In contrast to the reaction of the cationic $[Re(CO)_6]^+$ with azide ion[96], the reaction of $Re(CO)_3L_2Cl$ with azide ion yields $Re(CO)_3L_2N_3$ [98].

$mer\text{-}Re(CO)_3L_2Cl + N_3^- \rightarrow mer\text{-}Re(CO)_3L_2N_3 + Cl^-$
$(L = PMe_2Ph, PMePh_2)$

The reaction of azide ion with $Re(CO)_5Cl$ is reported to yield the diamagnetic complex, $[Re(CO)_3(N_3)(NCO)]^-$, which reacts readily with triphenylphosphine, L, to give $Re(CO)_3(L)_2NCO$ and $Re(CO)_3L_2N_3$ [100].

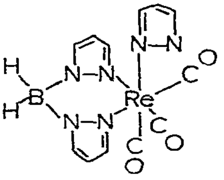
The nonionic, diamagnetic complexes *fac*-$Re(CO)_3(NH_3)_2Cl$ and *fac*-$Re(CO)_3(NH_2C_6H_5)_2Cl$ result when $Re(CO)_5Cl$ is treated with ammonia and aniline respectively in benzene[81,97]. The observed number of $\nu(CO)$ bands for $Re(CO)_3(NH_3)_2Cl$ is consistent with the *fac* isomer (XI).

$Re(CO)_4(NH_3)Cl$ is formed when $Re(CO)_5Cl$ and ammonia react at 33° [81]. The expected stoichiometric amounts of carbon monoxide are not liberated in these reactions and it is suggested that formamide and formanilide result. Reaction of piperidine or tetramethylethylenediamine with $Re(CO)_5Cl$ in diglyme also yield disubstituted complexes $Re(CO)_3L_2Cl$ [78].

4. *N-Heterocyclic and molecular nitrogen complexes*

The nitrogen heterocycles pyridine[18,97,101–103], γ-picoline[103], 2,2′-bipyridine[99,101] and 1,10-phenanthroline[102] react readily with $Re(CO)_5X$ to yield *fac*-$Re(CO)_3L_2X$ or $Re(CO)_3(L\text{–}L)X$. The monosubstituted complex *cis*-$Re(CO)_4(C_5H_5N)X$ results from the reactions of $[Re(CO)_4X]_2$ with pyridine[79].

Potassium dihydrodipyrazolylborate reacts with $Re(CO)_5Br$ or $Re_2(CO)_{10}$ to yield (XXIV)[104]. It is suggested that pyrazole results from a disproportionation of a complex, rather than an uncomplexed, $[H_2B(N_2C_3H_3)_2]^-$ unit. The phosphite $CH_3C(CH_2O)_3P$ reacts with (XXIV) to displace the pyrazole and the carbon monoxide *trans* to the pyrazole.



XXIV

A molecular nitrogen complex of rhenium presumably results when a rhenium benzoyl–hydrazido complex is chromatographed on silica gel[105,106].

$$Re(PPh_3)_2(N_2COPh)Cl_2 + 2CO \rightarrow Re(PPh_3)_2(CO)_2(N_2COPh)Cl_2 \xrightarrow{\text{Silica gel}} Re(PPh_3)_2(CO)_2N_2Cl + \text{other products}$$

The molecular nitrogen was detected by the presence of three absorptions at 2105, 2020 and 1920 cm^{-1} which are found at 2060, 2000 and 1930 cm^{-1} in the ^{15}N analog. Oxidation of the molecular nitrogen complex with chlorine yields two moles of carbon monoxide and one mole of nitrogen[105].

5. *Phosphorus and arsenic donor complexes*

Triphenylphosphine[79,99,103], diphenylethylphosphine[103] and tri-n-butylphosphine[103] readily cleave the halogen bridges in $Re_2(CO)_8X_2$ (X = Cl, Br, I) to yield *cis*-$Re(CO)_4LX$ complexes. Further reaction of $Re(CO)_4LX$ or the reaction of $Re(CO)_5X$ with excess ligands yields the well known $Re(CO)_3L_2X$ complexes. These tricarbonyl derivatives are reported for triphenylphosphine[80,101,103], diphenylethylphosphine[103], diphenylmethylphosphine[78], diphenylphosphine[78], tris(dimethylamino)phosphine[78], triphenylphosphite[80], triphenylarsine[101] and the chelating ligands diphos[80,99] and diars[99,107]. The *fac* isomer (XI), has been assigned to all these $Re(CO)_3L_2X$ complexes except the $P(NMe_2)_3$ complex which is the *mer* isomer (XII)[78]. *fac*-$Re(CO)_3(PPh_3)_2I$ has also been converted to the *mer* isomer by heating to 150° [80].

Several mixed phosphine–pyridine complexes $Re(CO)_3LL'X$ have been reported in conjunction with a kinetic study[103]

$$Re(CO)_4LX + L' \rightarrow fac\text{-}Re(CO)_3LL'X + CO$$

L	PPh_3	C_5H_5N	PPh_3	PPh_2Et	P-n-Bu_3
L'	C_5H_5N	PPh_3	Py	Py	PPh_3
X	Cl	Br	Br	Br	Br

Although substitution of more than two CO groups is difficult, the reaction of $Re(CO)_3[P(OPh)_3]_2I$ with excess ligand has resulted in $Re(CO)_2L_3I$ [80]. Similarly evacuated sealed tube reactions of diphos with $Re(CO)_5I$ yield dicarbonyl complexes. These cationic complexes yield monocarbonyl complexes when treated with an excess of diphos at 270°.

$$Re(CO)_5I + \text{diphos} \xrightarrow{X^-} [Re(CO)_2(\text{diphos})_2]^+X^-$$

$$(X = I^-, Cl^-, ClO_4^-, NO_3^-, BPh_4^-, SnCl_3^-)$$

Additional monocarbonyl complexes $Re(CO)(\text{diars})_2X$ (X = Cl, Br, I) are obtained from the treatment of $Re(CO)_3(\text{diars})X$ with excess ligand in sealed tubes at 270° [107]. These monocarbonyl complexes are oxidized by chlorine and bromine to yield seven coordinate ionic complexes. Similar oxidation reactions are discussed in section IV-B.

$$Re(CO)(\text{diars})_2X + 2X_2 \rightarrow [Re(CO)(\text{diars})_2X_2]X_3^-$$

The potentially terdentate ligand 1,1,1-tris(dimethylarsinomethyl)ethane (triars) reacts with $Re(CO)_5Cl$ to yield *fac*-$Re(CO)_3(\text{triars})Cl$ in which the ligand functions as a bidentate ligand[108].

Tetraphenyldiphosphine or -arsine react with $Re(CO)_5X$ to yield dimeric complexes which are presumably bridged by the bidentate ligand[109]. These dimeric complexes exhibit four $\nu(CO)$ bands and are assigned structure (XV). The presence of four $\nu(CO)$ bands is surprising in light of the five observed for $Re_2(CO)_6(PPh_3)_2(SePh)_2$ [110] and the three observed for the halogen bridged complexes $Re_2(CO)_6L_2X_2$. Dimeric tetracarbonyl complexes with bridging PPh_2 groups have been isolated from $Re(CO)_5X$ with $[PPh_2]^-$ [109] and $Me_3SiP(Ph)_2$ [111].

$$2Re(CO)_5X + L{-}L \rightarrow Re_2(CO)_6L_2X_2 + 4CO$$

$$(X = Cl, I,\ L{-}L = P_2Ph_4, As_2Ph_4)$$

$$2Re(CO)_5Cl + 2KPPh_2 \xrightarrow[\text{THF}]{20^\circ} Re_2(CO)_8(PPh_2)_2$$

$$2Re(CO)_5Br + 2Me_3SiPPh_2 \xrightarrow[\text{DME}]{60^\circ} Re_2(CO)_8(PPh_2)_2$$

Hydridopentacarbonylrhenium reacts with PPh_3, $P(OPh)_3$, and PEt_3 under mild conditions to yield *cis*-$Re(CO)_4LH$ [112]. Under more rigorous conditions tricarbonyl complexes result.

$$Re(CO)_5H + L \xrightarrow[140°]{\text{evac. sealed tube}} mer\text{-}Re(CO)_3L_2H$$

($L = PPh_3, PEt_3$)

$Re(CO)_3(PPh_3)_2H$ has also been prepared by carbonylating $Re(PPh_3)_3H_5$ [113]. With the polydentate ligands, 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylphosphino)-methane and 1,1,1-tris(diphenylphosphinomethyl)ethane complexes of the type *fac*-$Re(CO)_3(L{-}L)H$ are formed[112].

The reactions of phosphines and arsines with $[Re(CO)_6]^+$ are summarized in the following equations. The IR spectra of the cationic complexes confirm the expected *cis*

$[Re(CO)_6]ClO_4 + \text{triars} \rightarrow [Re(CO)_3(\text{triars})]ClO_4$ (ref. 108)

$[Re(CO)_6]ClO_4 + \text{diphos} \rightarrow [Re(CO)_4(\text{diphos})]ClO_4$ (ref. 78)

$[Re(CO)_6]ClO_4 + PPh_3 \rightarrow Re(CO)_3(PPh_3)_2Cl$ (ref. 78)

substitution. The reaction involving triphenylphosphine, however, is unusual and yields the well known *mer*-$Re(CO)_3(PPh_3)_2Cl$. Studies with ^{36}Cl labeled perchlorate confirm that the source of the chlorine is the perchlorate ion. Tetracarbonyl cationic complexes analogous to $[Re(CO)_4(\text{diphos})_2]^+$ have been reported from carbonylation reactions (section IV-B), from the reaction of HCl with $Re(CO)_3L_2CO_2R$ complexes (section II-A), and from the reaction of $Re(CO)_5Cl$ with triphenylphosphine in an evacuated sealed tube[81].

6. *Oxygen, sulfur and selenium donor complexes*

Oxygen donor ligands react with $Re_2(CO)_8Cl_2$ [114] and $Re(CO)_5X$ ($X = Cl, Br, I$)[115] to yield disubstituted, tricarbonyl complexes.

$Re_2(CO)_8Cl_2 + 4L \rightarrow 2\,fac\text{-}Re(CO)_3L_2Cl + CO$

($L = Ph_3PO, C_5H_5NO$)

$Re(CO)_5X + 2L \rightarrow fac\text{-}Re(CO)_3L_2X + 2CO$

($X = Cl, Br, I$; $L = C_5H_5NO, Ph_3PO$) ($L_2 = \text{bipyO}_2, \text{diphosO}_2$)

Mild, bridge splitting reactions of diethylsulfur, -selenium, and -tellurium ligands with $Re_2(CO)_8Cl_2$ are observed to yield *cis*-$Re(CO)_4LCl$ complexes[114]. With an excess of ligand in refluxing CCl_4 the $Re(CO)_3L_2Cl$ complexes are formed.

$Re(CO)_3L_2X$ ($L = Et_2S, Et_2Se, n\text{-}Bu_2Te$; $X = Cl, Br, I$) have also been reported from the reaction of $Re(CO)_5X$ with excess ligand[116]. These $Re(CO)_3L_2X$ complexes, except the case where L is $n\text{-}Bu_2Te$, are assigned a *fac* configuration (XI). Infrared evidence suggests that $Re(CO)_3(n\text{-}Bu_2Te)_2Cl$ exists in both the *fac*- (XI) and *mer*- (XII) forms.

The bidentate ligand 2,5-diselenohexane reacts with $Re(CO)_5X$ ($X = Cl, Br$) to yield complexes of the type $Re(CO)_3L{-}LX$ [117].

Halogen bridged complexes of the stoichiometry $\mathrm{Re_2(CO)_6L_2X_2}$ result from the reaction of $\mathrm{Re(CO)_5X}$ with sulfur and selenium ligands[116]. Three ν(CO) bands are observed

$$2\mathrm{Re(CO)_5X} + 2\mathrm{L} \rightarrow \mathrm{Re_2(CO)_6L_2X_2}$$

$$(\mathrm{L = SPh_2, SeEt_2, SePh_2;\ X = Cl, Br, I})$$

for these dimeric complexes and structure (XIV) assigned. Ligand displacement reactions with tetrahydrothiophene, tetrahydrofuran and pyrolidine yield both $\mathrm{Re(CO)_3L_2X}$ and $\mathrm{Re_2(CO)_6L_2X_2}$ complexes.

$$\mathrm{Re_2(CO)_6L_2X_2} + \mathrm{L} \longrightarrow \left[\begin{array}{ll} \rightarrow \mathrm{Re_2(CO)_6L_2X_2} & (\mathrm{L = THF, THT}) \\ \rightarrow \mathrm{Re(CO)_3L_2X} & (\mathrm{L = THT, C_4H_9N}) \end{array}\right.$$

$$(\mathrm{L = SPh_2, SePh_2})$$
$$(\mathrm{X = Cl, Br})$$

$\mathrm{Re_2(CO)_6(SePh_2)_2I_2}$ reacts with pyrolidine to yield the cation $[\mathrm{Re(CO)_3(C_4H_9N)_3}]^+$ [116].

If $\mathrm{Re_2(CO)_6(SPh_2)_2Cl_2}$ is heated in a high vacuum, diphenylsulfide is eliminated leaving a complex of the stoichiometry $[\mathrm{Re(CO)_3Cl}]_x$ [118]. The complex is assigned a halogen-bridged structure although its insoluble nature prevents an accurate molecular weight determination. An analogous bromine complex has been prepared by heating $\mathrm{Re(CO)_5Br}$ in an inert solvent at 130° for 48 h[119]. The infrared spectrum of $[\mathrm{Re(CO)_3Br}]_x$ is similar to that reported for $[\mathrm{Re(CO)_3Cl}]_x$ and both complexes may have the same structure.

Oxygen donor ligands readily react with $[\mathrm{Re(CO)_3Cl}]_x$ to yield monomeric $\mathrm{Re(CO)_3L_2Cl}$ and dimeric $\mathrm{Re_2(CO)_6L_2Cl_2}$ complexes[120]. Dimeric molecules are reported in which L is isopropyl alcohol, isobutyl alcohol, isopropyl ether, cyclohexanone, acetophenone, benzophenone and diacetyl. With acetone the monomeric complex $\mathrm{Re(CO)_3L_2Cl}$ is obtained. Ethylene glycol, dioxane, diacetyl, benzil, acetylacetone, benzoylacetone and dibenzoylmethane function as chelating bidentate ligands and yield complexes of the type $\mathrm{Re(CO)_3L_2Cl}$.

The reaction of alkoxides with $[\mathrm{Re(CO)_6}]^+$ and $[\mathrm{Re(CO)_4L_2}]^+$ has been discussed in section II-A.

Bromopentacarbonylrhenium(I) reacts with silver perfluorocarboxylates to yield pentacarbonyl complexes[121].

$$\mathrm{Re(CO)_5Br} + \mathrm{R_FCO_2Ag} \xrightarrow{\mathrm{CH_2Cl_2}} \mathrm{AgBr} + \mathrm{R_FCO_2Re(CO)_5}$$

$$(\mathrm{R_F = CF_3, C_2F_5, C_3F_7})$$

An infrared study of these complexes indicates that the monodentate carboxylate ligands are π donors and σ acceptors relative to $\mathrm{CH_3}$. $\mathrm{CF_3CO_2Re(CO)_5}$ has also been isolated from the reaction of $\mathrm{Re(CO)_5CH_3}$ with trifluoroacetic acid[122].

Dimeric tricarbonyl carboxylates of rhenium(I) are obtained by the reaction of

$Re(CO)_5Br$ with the sodium salts of acetic and benzoic acid[123]. These tricarbonyl complexes add carbon monoxide to yield pentacarbonyl complexes in which the

$$RCO_2Na + Re(CO)_5Br \rightarrow [RCO_2Re(CO)_3]_2$$

$$80^\circ \uparrow \ \downarrow 50^\circ, 300\text{ atm CO}$$

$$RCO_2Re(CO)_5$$

carboxylate ligand is monodentate. The phenyl complex also adds two molecules of triphenylphosphine to yield $Re(CO)_3(PPh_3)_2(PhCO_2)$. The structures of the dimeric complexes and $Re(CO)_3(PPh_3)_2(PhCO_2)$ are uncertain.

Organosulfur and selenium groups, RE, yield rhenium complexes of the types $RERe(CO)_5$, $[RERe(CO)_4]_2$, and $[RERe(CO)_3]_x$. The monomeric pentacarbonyl derivatives are isolated if R is an electron-withdrawing group. For example, the reaction of CF_3SAg with $Re(CO)_5Br$ yields $Re(CO)_5SCF_3$ and the sulfur bridged complex $[Re(CO)_4SCF_3]_2$ [124]. The analogous pentafluorophenylthio derivatives $Re(CO)_5SC_6F_5$ and $[Re(CO)_4SC_6F_5]_2$ have been reported from the reaction of $HRe(CO)_5$ with pentafluorothiophenol[125]. The pentacarbonyl derivatives readily lose CO to yield the RS bridged dimers.

If R is not electron withdrawing (e.g. Ph) CO is liberated and polynuclear complexes are isolated. The binuclear complex $[Re(CO)_4SPh]_2$ was first reported by heating $Re(CO)_5Cl$ with thiophenol in an evacuated sealed tube[126]. More recently the complex has been obtained from the reaction of $HRe(CO)_5$ and thiophenol at 20°C [125].

Bromopentacarbonylrhenium(I) reacts with thiols to form tricarbonyl derivatives $[Re(CO)_3SR]_x$ [125].

$$Re(CO)_5Br + RSH \xrightarrow[\text{reflux}]{\text{Cyclohexane}} [Re(CO)_3SR]_x + 2CO + HBr$$

(R = Me, Et, n-Bu, Ph)

Thus the MeS derivative was obtained from the sodium salt of methanethiol and $Re(CO)_5Br$. As expected, $Re(CO)_3(diphos)Br$ reacts with pentafluorothiophenol to yield $Re(CO)_3(diphos)SC_6F_5$.

Sulfur and selenium bridged complexes have also been reported in high yield from the reaction of organotin and silicon compounds with $Re(CO)_5X$.

$$Re(CO)_5Cl + \begin{matrix} R_2Sn(SR')_2 \\ \text{or} \\ R_3Sn(SR') \end{matrix} \xrightarrow{\text{diglyme}} [Re(CO)_3SR']_x \qquad \text{(ref. 127)}$$

$(R = R' = CH_3;\ R = Me, Ph;\ R' = n\text{-}Bu)$

$$Re(CO)_5Br + RSSi(Me)_3 \xrightarrow{\text{DME}} [Re(CO)_3SR]_x \qquad \text{(ref. 128)}$$

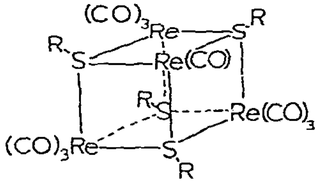
$$\mathrm{Re(CO)_5Cl + (Me)_3SnSSn(Me)_3 \xrightarrow{DME} [Re(CO)_4SSn(Me)_3]_2} \qquad \text{(ref. 129)}$$

$$\mathrm{Re(CO)_5X} + \begin{array}{c} \mathrm{Me_3SnSeR} \\ \text{or} \\ \mathrm{(Me)_2Sn(SeR)_2} \end{array} \xrightarrow{\mathrm{DME}} \mathrm{[Re(CO)_4SeR]_2} \qquad \begin{array}{c} \text{(ref. 130)} \\ \\ \text{(ref. 131)} \end{array}$$

(X = Cl, Br; R = Me, Et, Ph)

The tetracarbonyl derivative $[Re(CO)_4SeR]_2$ loses CO when pyrolyzed to yield $[Re(CO)_3SeR]_x$ complexes[130]. The trimethyltin group in $[Re(CO)_4SSn(Me)_3]_2$ can be replaced by a $Re(CO)_5$ group to give $Re(CO)_4SRe(CO)_5$ of unknown structure[129].

The $[Re(CO)_3SR]_x$ complexes were originally formulated as trimers but subsequent mass spectral data[132] and infrared data[133] indicated a tetrameric structure. The tetrameric structure (XXV) has not been established for $[Re(CO)_3SMe_3]_4$ by an X-ray crystallographic study[134]. It is assumed that the selenium analogs have similar structures.



XXV

The rhenium complexes $Re(CO)_4(PPh_3)Br$ and $Re(CO)_3(PPh_3)_2Cl$ react with organotin–sulfur or –selenium complexes according to the following scheme[110].

$$\begin{array}{c} \mathrm{2Re(CO)_3(PPh_3)_2Cl} \\ \text{or} \\ \mathrm{2Re(CO)_4(PPh_3)Br} \end{array} + \mathrm{2(Me)_3SnER \rightarrow [Re(CO)_3(PPh_3)_2ER]_2}$$

(E = S, Se; R = Me, Ph, *p*-MePh)

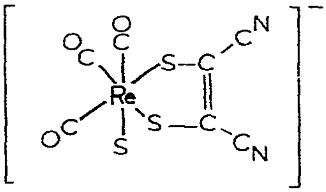
The displacement of triphenylphosphine by a sulfur donor is unusual. Abel suggests that the displacement of at least one carbon monoxide or triphenyl phosphine may be an essential step in the reactions utilizing alkyl- or arylthiotin reagents[110]. For the dimeric complexes five ν(CO) bands are observed. These data are considered indicative of structure (XV). The SePh bridged complexes containing triphenylphosphine are also obtained from the following reaction[110].

$$\mathrm{[Re(CO)_4SePh]_2 + 2PPh_3 \rightarrow [Re(CO)_3(PPh_3)SePh]_2}$$

With diphos, however, the reaction yields a monomeric complex analogous to $Re(CO)_3(diphos)SC_6F_5$ (vide supra[125]).

$$[Re(CO)_4SePh]_2 + 2diphos \rightarrow 2Re(CO)_3(diphos)SePh + 2CO$$

The unsaturated heterocycle 4,5-dicyano-2,2-dimethyl-1,3-dithia-2-stannacyclopentene has been used as a source of the *cis*-1,2-dicyanoethylene-1,2-dithiolate anion $[S_2C_2(CN)_2]^{2-}$ [128]. The stannacyclopentene reacts with $Re(CO)_5Br$ in refluxing methanol to yield $Re(CO)_4S_2C_2(CN)_2^-$ which may have structure (XXVI).



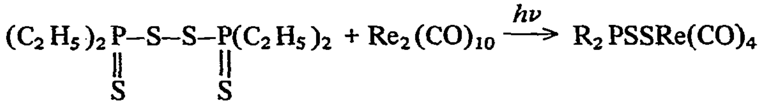
XXVI

Dithiocarboxylatotetracarbonyl derivatives of rhenium have been reported from insertion reactions with carbon disulfide (section II-C). The dithiobenzoatotetracarbonylrhenium(I) complex has also been isolated in low yield from the thiobenzoyl chloride and sodium pentacarbonylrhenate(I) [135]. The product apparently arises from a small amount of a $C_6H_5CSCl{-}S_2Cl_2$ adduct which persists in the thiobenzoylchloride.

Diorganodithiophosphinate complexes of rhenium are obtained by reaction of sodium diethyl- or diphenyldithiophosphinate with $Re(CO)_5Br$ [136,137].

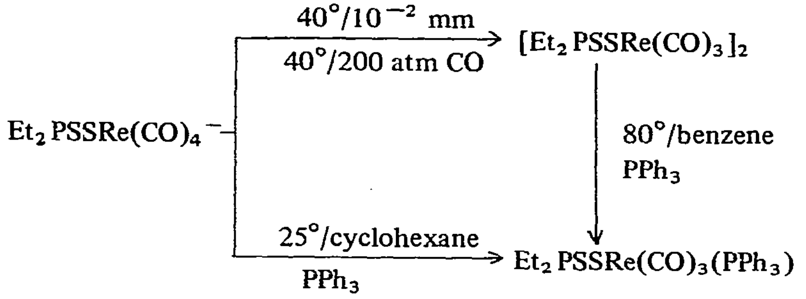
$$R_2PSSNa + Re(CO)_5Br \xrightarrow[\text{dioxane}]{60\text{–}90°} R_2PSSRe(CO)_4$$

$(R = C_2H_5, C_6H_5)$

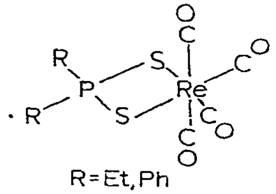


$$\underset{\underset{S}{\|}}{(C_2H_5)_2P}{-}S{-}S{-}\underset{\underset{S}{\|}}{P}(C_2H_5)_2 + Re_2(CO)_{10} \xrightarrow{h\nu} R_2PSSRe(CO)_4$$

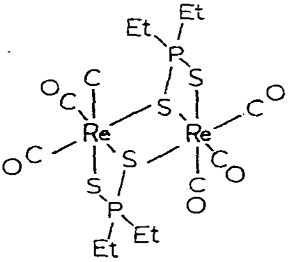
$(C_2H_5)_2PSSRe(CO)_4$ is also formed by photochemical reaction of bis(diethylthiophosphoryl)disulfide with $Re_2(CO)_{10}$. Carbon monoxide is reversibly eliminated by the ethyl derivative yielding the bimetallic $[(C_2H_5)_2PSSRe(CO)_3]_2$ which further reacts with triphenylphosphine to give $(C_2H_5)_2PSSRe(CO)_3P(C_6H_5)_3$. The phosphine derivative can also be obtained directly from $(C_2H_5)_2PSSRe(CO)_4$. The proposed structures for the



monomer and dimer are given by (XXVII) and (XXVIII). (XXVIII) is similar to structure (XIV). The carboxylato complexes $[RCO_2Re(CO)_3]_2$ [123] and complexes $[RSS(H)Re(CO)_3]_2$ may be structurally related to (XXVIII).

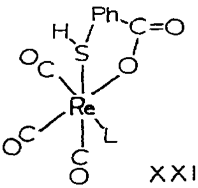


XXVII

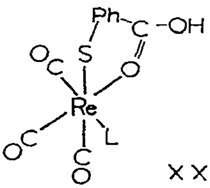


XXVIII

Hieber and Rohm[138] describe an extensive study on reactions of $Re(CO)_5Cl$ with organic compounds containing both nitrogen and sulfur atoms. These reactions are summarized in Table 4. In addition to the products listed in Table 4, $Re(CO)_5Cl$ reacts with thiosalicylic acid to yield an equilibrium mixture of tautomeric species. Heating of the complex [L = Et_2O] in benzene solution results in formation of bimetallic oxygen bridged species $Re(CO)_3[SH(CO_2)_2C_6H_4]_2$ (XXXI) which is also produced in the reaction between thiosalicylic acid and $Re(CO)_5Cl$ in benzene. When the complex (L = THF) is treated with OH^- and Ph_4As^+, the acidic proton is removed giving a compound of possible structure (XXXII). An analogous series to (XXXI), but with sulfur bridges, is obtained from the reactions of thiolactic acid and ethyl thiolactate with $Re(CO)_5Cl$.



XXIX



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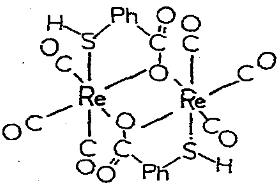
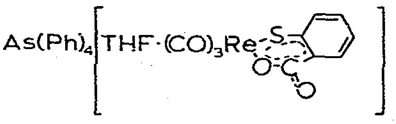


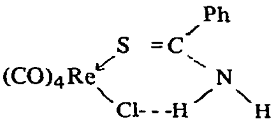
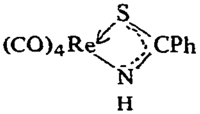
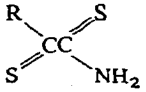
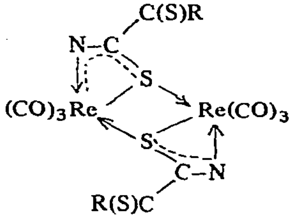
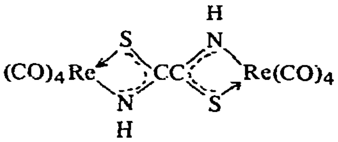
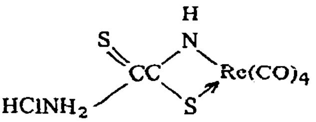
XXXI



XXXII

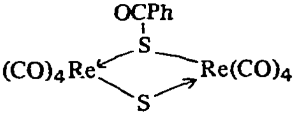
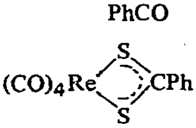
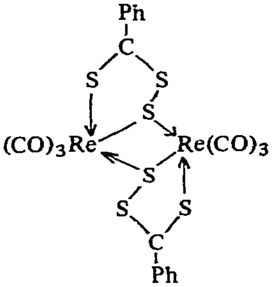
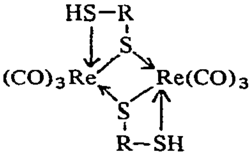
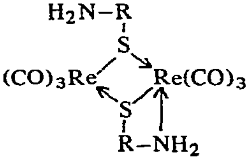
TABLE 4

REACTION PRODUCTS OF $Re(CO)_5Cl$ WITH BIDENTATE LIGANDS
A, excess ligand; B, 1/1 mole ratio of ligand to $Re(CO)_5Cl$; C, reflux 5 h in xylene.

Reaction	Ligand	Product	Remarks
1	$RC(S)NH_2$ ($R = NH_2$, Me, Ph)	$[R(NH_2)CS]_2Re(CO)_4$	A
2	$PhC(S)NH_2$		B
2a			B low yield
3			B
3a			low yield
3b			low yield

(Table continued)

TABLE 4 *(continued)*

4	PhC(O)SH		A
5	PhC(S)SH		A
5a			C
6	HSRSH (R = CH_2CH_2, 1,2-C_6H_3-4-Me)		A
7	H_2NRSH (R = C_2H_4, 1,2-C_6H_4)		A

7. Halide and pseudohalide complexes

Halide ions react with $Re(CO)_5X$ in an appropriate solvent at 80–120° to yield dihalotetracarbonylrhenates[139].

$$\left.\begin{array}{l} Re(CO)_5X + Y^- \\ \\ Re(CO)_5Y + X^- \end{array}\right. \rightarrow [Re(CO)_4XY]^- + CO$$

$$(X, Y = Br^-, I^-)$$

Further reaction of $Re(CO)_5I$ with I^- for 8 h yields a tricarbonyl complex. Monomeric tricarbonyl complexes and dimeric complexes result from the following reaction[140]. Additional dimeric complexes are also obtained from the reaction of $Re(CO)_5X$ with halide

$$\begin{array}{l} [Re_2(CO)_6L_3]^- + HX \\ (L = H, EtO, i\text{-}PrO) \end{array} \longrightarrow \begin{cases} [Re(CO)_3X_3]^{2-} \quad (X = Cl, Br, I) \\ [Re_2(CO)_6X_4]^{2-} \quad (X = Cl, Br) \end{cases}$$

ions[139]. Infrared evidence suggests that the $[Re(CO)_3X_3]^{2-}$ complexes have C_{3v} symmetry

$$Re(CO)_5X + X^- \rightarrow [Re_2(CO)_7X_3]^-$$

$$(X = Cl, Br)$$

and that dimeric complexes are halogen bridged of type (XIV) or (XV).

The reaction of $Re(CO)_5Br$ with KSCN in methanol results in $[Re(CO)_3(NCS)_3]^{2-}$ with no trace of $[Re(CO)_4(NCS)_2]^-$ [141]. This is in contrast with the analogous manganese reaction in which there is no evidence for further substitution of $[Mn(CO)_4(SCN)_2]^-$ [141] The reaction of $Re(CO)_4(PPh_3)Br$ and $Re(CO)_3(PPh_3)_2Br$ with KSCN in diglyme also yields $[Re(CO)_3(SCN)_3]^{2-}$. The infrared data support a *fac* substituted (C_{3v}) complex with *N*-bonded thiocyanato groups.

The ionic complex $[Re_2(CO)_2(NCS)_{10}]^{3-}$ has been reported and it has been suggested that it consists of $[Re(NCS)_6]^{2-}$ and $Re(CO)_2(NCS)_4^-$ [142].

In contrast with KSCN, KCN reacts with $Re(CO)_5Cl$ to give $[Re(CO)_4(CN)_2]^-$ [81]. This product was also prepared from $[Re(CO)_6]^+$ and NaCN in acetone[96]. It is interesting that this latter reaction does not yield the yet unknown $Re(CO)_5CN$. Further substitution, however, is possible and both $[Re(CO)_3(CN)_3]^{2-}$ and $[Re(CO)_2(CN)_4]^{3-}$ have been reported[92].

$$Re(CO)_5Cl + 3KCN \xrightarrow[EtOH]{\text{sealed tube}} 2CO + KCl + K_2[Re(CO)_3(CN)_3]$$

$$[Re(CO)_2(diphos)_2]Cl \xrightarrow[NaCN]{EtOH} [Re(CO)_2(CN)_4]^{3-} + KCl + 2(diphos)$$

The infrared spectra of $[Re(CO)_3(CN)_3]^{2-}$ and $[Re(CO)_2(CN)_4]^{3-}$ both display two $\nu(CO)$ bands consistent with structures of C_{3v} and C_{2v} symmetry, respectively.

The neutral ammonia substituted product $Re(CO)_3(NH_3)_2CN$ results from the reaction of $Re(CO)_5Cl$ with KCN and ammonia in a sealed tube at 120° or from the reaction of $Re(CO)_4(NH_3)(CONH_2)$ with ammonia at 120° [92,93]. The infrared spectrum of the complex displays 2 $\nu(CO)$ bands and one $\nu(CN)$ band when recorded in ethanol[92]. A *fac* arrangement for the CO groups is suggested and the absence of the third expected $\nu(CO)$ band explained by considering pseudo C_{3v} symmetry. The ionic product $[Re(CO)_3(NH_3)(CN)_2]^-$ has been reported[92] from the reaction of $Re(CO)_5Cl$ with KCN and NH_3.

B. Carbonylation of rhenium complexes

The tricarbonyl complexes $Re(CO)_3L_2Cl$ react with carbon monoxide to yield ionic tetracarbonyl complexes[143]. These tetracarbonyl complexes are presumably identical to

$$Re(CO)_3L_2Cl + CO \xrightarrow[90^\circ\ \text{metal halide}]{300\ \text{atm}} [Re(CO)_4L_2]^+ + Cl^-$$

(metal halide = $AlCl_3$, $FeCl_3$, $ZnCl_2$)

(L = PPh_3, *o*-phen)

those isolated directly from $Re(CO)_5X$ with ligands such as triphenylphosphine[81].

Rhenium hydrido-phosphine complexes have been reported to carbonylate according to the following equations:

$$ReH_2(PPh_3)_2acac + CO \xrightarrow{EtOH} Re(CO)_2(PPh_3)_2acac \qquad \text{(ref. 144)}$$

$$ReH_4(PPh_3)_2I + CO \xrightarrow{C_6H_6} Re(CO)_3(PPh_3)_2I \qquad \text{(ref. 113)}$$

$$ReH_4(PPh_3)_2I + PPh_3 \xrightarrow{EtOH} Re(CO)(PPh_3)_3H_2I \qquad \text{(ref. 113)}$$

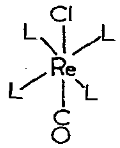
$$ReH_5(PPh_3)_3 + CO \xrightarrow[120^\circ]{200\ \text{atm}} Re(CO)_3(PPh_3)_2H \qquad \text{(ref. 145)}$$

Little is known about the structure of $Re(CO)_2(PPh_3)_2acac$ but from the data given the CO groups are probably in a *cis* arrangement. The $Re(CO)_3(PPh_3)_2I$ complex is assigned a *mer* structure[113]. From the data given $Re(CO)_3(PPh_3)_2H$ also appears to be the *mer* configuration which has also been reported from the reaction of $Re(CO)_5H$ with triphenylphosphine[112]. The hydridocarbonyl $Re(CO)(PPh_3)_3H_2I$ readily reacts with HCl, I_2 or O_2 to yield the well known $Re(CO)_3(PPh_3)_2I$ [113].

Tricarbonyl and dicarbonyl derivatives, $Re(CO)_3(PPh_3)_2X$ and $Re(CO)_2(PPh_3)_2X$, have been reported from the carbonylation of $Re(PPh_3)Cl_3$ and $Re(PPh_3)_2Br_2$ [146] ($Re(PPh_3)_2Br_2$ may be $Re(O)(PPh_3)_2(OEt)Br_2$ [147]). Little is known about the structures of these complexes but the dicarbonyl complexes may be five coordinate and the tricarbonyl derivatives are most likely of structure (XI) or (XII).

The octahedral *mer*-$Re(PMe_2Ph)_3X_3$ (X = Cl, Br) readily carbonylates in 2-methoxyethanol to yield two isomers, (XI) and (XII), of $Re(CO)_3(PMe_2Ph)_2X$ [148]. The *mer* configuration also results from the carbonylation of *trans*-$Re(PPh_3)_2Cl_4$ or the reaction of *mer*-$Re(PMe_2Ph)_3Cl_3$ with formic acid. Carbonylation in 2-diethylaminoethanol yields $Re(CO)(PMe_2Ph)_4Cl$ which is assigned structure (XXXIII) on the basis of its NMR spectrum. Under reducing conditions *mer*-$Re(PMe_2Ph)_3Cl_3$ yields a dicarbonyl derivative in which the phosphines are presumably in a *mer* relationship. The complexes

$$mer\text{-}Re(PMe_2Ph)_3Cl_3 \xrightarrow[CO(THF)]{Na(Hg)} Re(CO)_2(PMe_2Ph)_3Cl$$



XXXIII

$Re(CO)_3(PMe_2Ph)_2Cl$ are oxidized by chlorine in carbon tetrachloride to yield seven coordinate complexes of uncertain structure[148].

$$Re(CO)_3(PMe_2Ph)_2Cl + Cl_2 \rightarrow Re(CO)_2(PMe_2Ph)_2Cl_3 + CO$$

Monocarbonyl derivatives $Re(CO)(PMe_2Ph)_3Cl_3$ are obtained from the chlorine oxidation of $Re(CO)_2(PMe_2Ph)_3Cl$ or $Re(CO)(PMe_2Ph)_4Cl$ and from the carbonylation of *mer*-$Re(PMe_2Ph)_3Cl_3$ in ethanol. These oxidation reactions are in contrast to that of $Re(CO)(diars)_2X$ with halogens which yield the ionic $[Re(CO)(diars)_2X_2]^+X_3^-$ [107].

C. Substitution reactions of dirhenium decacarbonyl

Dirhenium decacarbonyl reacts with PMe_2Ph and $PMePh_2$ to yield dimeric, diamagnetic complexes $Re_3(CO)_9L$ in which the metal–metal bond is retained[149]. Infrared evidence suggests that $PMePh_2$ substitutes *trans* to the metal–metal bond and PMe_2Ph *cis*. Both complexes react with dry HCl to yield $Re(CO)_5Cl$ and $Re(CO)_4LCl$. The $Re(CO)_4(PMe_2Ph)Cl$ is a *cis* and $Re(CO)_4(PMePh_2)Cl$ is a *trans* arrangement.

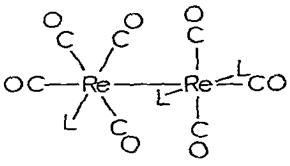
Dimeric diamagnetic complexes of the stoichiometry $Re_2(CO)_8L_2$ are obtained if phosphines are reacted with $Re_2(CO)_{10}$ [149–154]. The complex $Re_2(CO)_8(PPh_3)_2$ has been assigned a structure in which the substitution is *trans* to the metal–metal bond[150]. The analogous complexes containing PMe_2Ph and $PMePh_2$ are assigned structures in which the substitution is *cis* to the metal–metal bond[149,154]. The reaction of iodide ion with $Re_2(CO)_{10}$ presumably yields an analogous complex $[Re_2(CO)_8I_2]^{2-}$ in which the substitution is *trans* to the metal–metal bond[139].

Kinetic studies of reactions of $Re_2(CO)_{10}$ with triphenylphosphine to yield $Re_2(CO)_9PPh_3$ and $Re_2(CO)_8(PPh_3)_2$ have been interpreted to indicate that the reactions occur mainly through a CO bridged intermediate $(CO)_4ReCORe(CO)_5$ [155]. For substitution an additional CO group is lost, presumably from the metal to which the ligand is bonded.

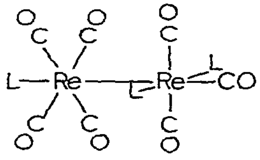
The $Re_2(CO)_8L_2$ complexes are oxidized by halogens or hydrogen halides to yield both *cis*- and *trans*-$Re(CO)_4LX$ complexes. The stereochemistry of the resulting rhenium(I) complexes reflects the arrangement of the original $Re_2(CO)_8L_2$ complex. Thus *trans*-$Re(CO)_4LX$ complexes are obtained from $Re_2(CO)_8(PPh_3)_2$ [150,152] and *cis* complexes from $Re_2(CO)_8(PMe_2Ph)_2$ [154] and $Re_2(CO)_8(PMePh_2)_2$ [149].

Dimeric, diamagnetic complexes of the type $Re_2(CO)_7L_3$, have been isolated from photochemical reactions of dirhenium decacarbonyl with PMe_2Ph [154], $PMePh_2$ [149] and

$AsMe_2Ph$[154]. The three ligands produce one isomer which exhibits six IR active ν(CO) bands and which reacts with halogens to yield *mer*-$Re(CO)_3L_2X$ and *cis*-$Re(CO)_4LX$. This chemical evidence along with the coupling patterns in the NMR spectra is attributed to structure (XXXIV). In addition $PMePh_2$ yields another isomer of $Re_2(CO)_7L_3$ which exhibits five ν(CO) bands and gives *mer*-$Re(CO)_3L_2Cl$ and *trans*-$Re(CO)_4LCl$ when reacted with dry HCl[149]. The second isomer is assigned structure (XXXV).

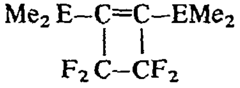


XXXIV



XXXV

The bidentate phosphine and arsine ligands f_4fos and f_4fars react with dirhenium



$$\begin{array}{l} Me_2E{-}C{=}C{-}EMe_2 \\ \quad\;\;\, | \quad\; | \\ \quad F_2C{-}CF_2 \end{array}$$

($E = P = f_4fos$; $E = As = f_4fars$)

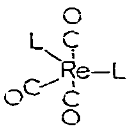
decacarbonyl in refluxing xylene to yield $f_4fosRe_2(CO)_8$ and $f_4farsRe_2(CO)_8$[156]. Structures with a metal–metal bond in which f_4fos and f_4fars are bridging groups are suggested. The structure has been confirmed by an X-ray study for the analogous manganese compound $f_4farsMn_2(CO)_8$[156]. Treatment of $f_4fosRe_2(CO)_8$ and $f_4farsRe_2(CO)_8$ with iodine in dichloromethane yields complexes of the type $L[Re(CO)_4I]_2$ which is further evidence for bridging ligands.

The monomeric, paramagnetic complex $Re(CO)_5PMe_2Ph$ has been isolated in low yield from the reaction of $Re_2(CO)_{10}$ with 2 moles of PMe_2Ph[149]. The infrared spectrum of the unusual complex is consistent with a structure of C_{4v} symmetry.

With reaction conditions that are more severe than those required for $Re_2(CO)_8L_2$ complexes, monomeric complexes $Re(CO)_3L_2$ are isolated. For example the $PMePh_2$

$$Re_2(CO)_{10} + 2PMePh_2 \xrightarrow[\text{Cyclohexane}]{h\nu/12\text{ h}} Re(CO)_3(PMePh_2)_2$$

complex is isolated in 2% yield from a photochemical reaction[149]. The analogous PPh_3[150], PMe_2Ph[154], $AsMe_2Ph$[154] and diphos[150] complexes have been reported. Three ν(CO) bands are reported for these paramagnetic complexes which are consistent with either trigonal bipyramidal or square pyramidal structures. Structure XXXVI is suggested for $Re(CO)_3(PMe_2Ph)_2$.



XXXVI

Complexes of the type $[Re(CO)_3L_2]_2$, L = PPh_3, $P(OPh)_3$, have also been reported[77,150]. These are dimeric and diamagnetic in the solid state but paramagnetic and monomeric in solution. The complex containing PPh_3 exhibits a single ν(CO) band when measured in solution[150]. This is consistent with a D_{3h}, trigonal bipyramidal structure. $[Re(CO)_3(PPh_3)_2]_2$ has also been obtained by heating $Re(CO)_3(PPh_3)_2H$ under vacuum[145]. The chelating diphosphine (diphos) yields a complex, $[Re(CO)_3(diphos)]_2$, which is diamagnetic in both the solid and solution phase[150]. A rhenium–rhenium bonded species with *cis* CO groups is suggested.

The tricarbonyl complexes $Re(CO)_3L_2$ and $[Re(CO)_3L_2]_2$ are oxidized by halogens or halogen containing molecules to yield tricarbonyl complexes $Re(CO)_3L_2X$ [149,150,154]. All three of the possible geometrical isomers, (XI), (XII) and (XIII) have been isolated as evidenced by IR and NMR studies. The complexes $Re(CO)_3(PMePh_2)_2X$ [149] and $Re(CO)_3(PPh_3)_2X$ [150] are assigned the *mer* configuration (XII). The analogous PMe_2Ph complex, however is assigned the *fac* structure[149]. $Re(CO)_3$(diphos)(I) is the only complex considered to have structure (XIII)[150].

The nitrogen donor ligands pyridine, L, and 2,2′-bipyridyl, L_2, replace two CO groups and form $[Re(CO)_3L_2]_n$ [102]. Little information about these complexes is available.

$Re_2(CO)_{10}$ and diphos yield paramagnetic $Re(CO)_2(diphos)_2$ and $Re(CO)(diphos)_2$ when allowed to react at high temperatures[150]. $Re(CO)_2(diphos)_2$ is monomeric in solution and exhibits two strong ν(CO) bands. An octahedral structure with C_2 molecular symmetry is suggested which would be dissymmetric. $Re(CO)_2(diphos)_2$ and $Re(CO)_5PMe_2Ph$ [149] are unusual because they do not comply with the 18 electron rule. $Re(CO)_2(diphos)_2$ reacts with three equivalents of iodine to yield $Re(CO)_2(diphos)[Ph_2P(CH_2)_2P(I)_2Ph_2]I$ [150]. It is suggested that one of the four phosphorus atoms is oxidized to a P^V diiodide. $Re(CO)(diphos)_2$ reacts with iodine to yield $Re(CO)(diphos)_2I$.

The dicarbonyl complex $Re(CO)_2(PMe_2Ph)_3Cl$ has been isolated from the reaction of $Re_2(CO)_{10}$ with PMe_2Ph in chlorinated solvents[154]. The chlorine presumably results from the solvent. The reaction of $Re_2(CO)_7(PMe_2Ph)_3$ with excess bromine also yields a monocarbonyl complex $Re(CO)(PMe_2Ph)_2Br_3$.

Liquid dinitrogen tetroxide reacts with $Re_2(CO)_{10}$ to yield $Re(CO)_5NO_3$ [157]. The nitrate group functions as a unidentate ligand so that the structure is octahedral.

$$Re_2(CO)_{10} + 2N_2O_4 \rightarrow 2Re(CO)_5NO_3 + 2NO$$

The reaction between $Re_2(CO)_{10}$ and $SbCl_5$ has been reported[158]. The product has been formulated as either an ionic derivative $[(CO)_5ReClRe(CO)_5]SbCl_6$ or a covalent derivative $SbCl_5[Re(CO)_5Cl]_2$. The reactions of $Re_2(CO)_{10}$ with silanes and stannanes have been discussed in section II-B.

The reaction of $Re_2(CO)_{10}$ with mesoporphyrin(IX) dimethyl ester yields two novel products[159]. One has been characterized as μ-mesoporphyrin(IX)dimethylesteratobis[tricarbonylrhenium(I)]. The complex is diamagnetic and a parent peak is observed at *m/e* 1130 in the mass spectrum. (Monohydrogenmesoporphyrin(IX)dimethylesterato)tricarbonylrhenium(I) has also been isolated. This product exhibits a parent peak in the mass spectrum (*m/e* 862) and a high field peak in the NMR at τ 14.9. The following reaction scheme is suggested.

$$\tfrac{1}{2}Re_2(CO)_{10} + PH_2 \rightarrow Re(PH)(CO)_3$$

$$Re(PH)(CO)_3 + \tfrac{1}{2}Re_2(CO)_{10} \rightarrow (CO)_3RePRe(CO)_3$$

(P = porphyrin dianion)

V. TRANSITION METAL DERIVATIVES

The synthesis of manganese rhenium decacarbonyl has been reported by the following methods[160,161]:

$$NaMn(CO)_5 + Re(CO)_5Cl \xrightarrow{THF} MnRe(CO)_{10} + NaCl$$

$$Mn(CO)_5Br + NaRe(CO)_5 \xrightarrow{THF} MnRe(CO)_{10} + NaBr$$

The compound was characterized by its infrared spectrum, but in a later report Kaesz and coworkers[162] showed that the product from these reactions is a mixture of $MnRe(CO)_{10}$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ which gives an identical infrared spectrum to that originally reported. It was found that a high yield of $MnRe(CO)_{10}$ could be obtained from $NaMn(CO)_5$ and $Re(CO)_5Br$ or by irradiation of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ with UV light in n-hexane[163]. In other related reactions, the compounds $Cp(CO)_3MRe(CO)_5$ (M = Mo, W) were prepared from $NaM(CO)_3Cp$ and $Re(CO)_5Cl$ [164] while formation of the anions $[ReM(CO)_{10}]^-$ (M = Cr, Mo, W) result from the reaction of $NaRe(CO)_5$ with the Group VI metal carbonyls[165].

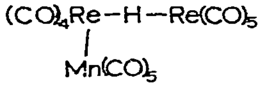
$$[Re(CO)_5]^- + M(CO)_6 \xrightarrow[160-170^\circ]{\text{diglyme}} [(CO)_5ReM(CO)_5]^- + CO$$

(M = Cr, Mo, W)

These anions are isolated as the yellow or orange tetraethylammonium salts.

$HRe_2Mn(CO)_{14}$ is obtained in low yield by acidification of a dry mixture of $NaMn(CO)_5$ and the salt obtained by treating $Re_2(CO)_{10}$ with $NaBH_4$ in tetrahydrofuran[166]. A single-crystal X-ray diffraction study shows that the metal atoms are in a nonlinear configuration

(XXXVII), the Re. . . .Re–Mn angle being 98° [167]. It is proposed that the hydrogen atom occupies a bridging position between the two rhenium atoms. In all probability, the previously discussed compound $HRe_3(CO)_{14}$ [67] will have this structure in the solid state.



$$\begin{array}{l}(CO)_4Re{-}H{-}Re(CO)_5\\ \;\;\;\;\;\;| \\ \;\;\;Mn(CO)_5\end{array}$$

XXXVII

A number of ionic compounds have been prepared from a rhenium carbonyl cation and a carbonylmetallate anion[35].

$$[Re(CO)_4L_2]^+ + [M(CO)_n]^- \rightarrow L_2(CO)_3ReM(CO)_n + CO$$

(L = CO, PPh_3, ½*o*-phen) (M = transition metal)

A list of the various salts prepared in this manner is given in Table 5. Thermal decomposition of the salt $[Re(CO)_6][Co(CO)_4]$ or its *o*-phenanthroline derivative $[Re(CO)_4(C_{12}H_8N_2)][Co(CO)_4]$ results in the loss of one carbon monoxide molecule and the formation of a rhenium–cobalt σ bond[168].

TABLE 5

BINUCLEAR MIXED METAL CARBONYL SALTS[35]

Salt	[Cation]X X	M[Anion] M	Solvent
$[Re(CO)_6][Co(CO)_4]$	$[AlCl_4]^-$	Na^+	H_2O
$[Re(CO)_6][V(CO)_6]$	$[AlCl_4]^-$	K^+	H_2O
$[Re(CO)_6][Fe(CO)_3NO]$	$[AlCl_4]^-$	Na^+	H_2O
$[Re(CO)_4(PPh_3)_2][Co(CO)_4]$	$[AlCl_4]^-$	Na^+	THF
$[Re(CO)_4(PPh_3)_2][V(CO)_6]$	$[AlCl_4]^-$	K^+	THF
$[Re(CO)_4(PPh_3)_2][Fe(CO)_3NO]$	$[AlCl_4]^-$	Na^+	THF
$[Re(CO)_4(PPh_3)_2][Mn(CO)_5]$	Cl^-	Na^+	THF
$[Re(CO)_4(C_{12}H_8N_2)][Co(CO)_4]$	$[Zn_2Cl_6]^{2-}$	Na^+	Me_2CO
$[Re(CO)_4(C_{12}H_8N_2)][Mn(CO)_5]$	Cl^-	Na^+	Me_2CO

$$[Re(CO)_6][Co(CO)_4] \xrightarrow{60^\circ} (CO)_5ReCo(CO)_4 + CO$$

$$[Re(CO)_4(C_{12}H_8N_2)][Co(CO)_4] \xrightarrow{90^\circ} (C_{12}H_8N_2)(CO)_3ReCo(CO)_4 + CO$$

When the anion is $[Mn(CO)_5]^-$, the conversion to a Re–Mn bond takes place spontaneously on dissolving the salt in THF at 0° [35]. This rhenium–manganese compound is also obtained from the reaction of $NaMn(CO)_5$ and the complex salt shown below[169].

$$[Re(CO)_4(o\text{-phen})]_2[Zn_2Cl_6]\cdot Me_2CO + NaMn(CO)_5 \xrightarrow{THF} (o\text{-phen})(CO)_3ReMn(CO)_5$$

Ultraviolet irradiation of an n-hexane solution of $Fe(CO)_5$ and $Re_2(CO)_{10}$ yields $Re_2Fe(CO)_{14}$ and the anion $[ReFe_2(CO)_{12}]^-$ [170]. $Re_2Fe(CO)_{14}$ has a simple four band ν(CO) spectrum which suggests a linear structure of D_{4h} symmetry (XXXVIII). The structure of the anion is considered to be derived from $Fe_3(CO)_{12}$ [171] by replacing the

$$(CO)_5Re{-}Fe(CO)_4{-}Re(CO)_5$$

XXXVIII

$Fe(CO)_4$ group with $[Re(CO)_4]^-$. This contention was verified when $[Re(CO)_5]^-$ was found to react with $Fe_3(CO)_{12}$ to give the expected anion $[ReFe_2(CO)_{12}]^-$ [172]. If this anion is treated with the oxidizing agent tropylium bromide, the novel hexanuclear complex $[ReFe_2(CO)_{12}]_2$ is formed which possibly is produced from the coupling of two $ReFe_2(CO)_{12}$ groups via the rhenium atoms. Irradiation of $MnRe(CO)_{10}$ and $Fe(CO)_5$ in n-hexane yields the compound $ReFeMn(CO)_{14}$ of unknown structure[163].

Several polynuclear complexes containing osmium and rhenium have been prepared. The thermally induced homolytic cleavage of $Re_2(CO)_{10}$ produces radicals which attack $Os_3(CO)_{12}$ resulting in the formation of $Re_2Os(CO)_{14}$ [173].

$$3Re_2(CO)_{10} + Os_3(CO)_{12} \xrightarrow[50\text{ h}]{250^\circ} 3(CO)_5ReOs(CO)_4Re(CO)_5$$

A linear structure is proposed for this compound similar to that postulated for the iron analog $Re_2Fe(CO)_{14}$ on the basis of their nearly identical infrared spectra. Acidification of the products from the reaction of $Os_3(CO)_{12}$ with $[Re(CO)_5]^-$ under various conditions lead to four different mixed metal hydrides; $HReOs_2(CO)_{12}$, $HReOs_3(CO)_{16}$, $HReOs_3(CO)_{15}$, and $H_3ReOs_3(CO)_{13}$ [174]. These compounds have complex infrared spectra and speculation on their structures is unwarranted pending the results of an X-ray diffraction study.

Complexes containing rhenium–Group IIB metal bonds have been synthesized[175]. $Hg[Re(CO)_5]_2$ can be prepared from the reaction of $NaRe(CO)_5$ with $Hg(CN)_2$ in aqueous solution or from the reaction of Me_2Hg with $HRe(CO)_5$. The compounds $M[Re(CO)_5]_2$ (M = Zn, Cd) are also prepared from $HRe(CO)_5$ and either $(Me)_2Zn$ or $(Me)_2Cd$. Other satisfactory methods of preparing the zinc and cadmium compounds include insertion of the corresponding metal into the Re–Re bond of $Re_2(CO)_{10}$, or by metal exchange with the mercury compounds.

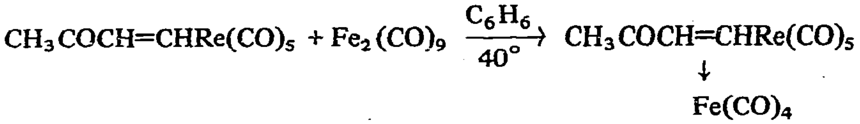
$$M + Re_2(CO)_{10} \xrightarrow[\text{reflux}]{\text{diglyme}} M[Re(CO)_5]_2$$

$$M + Hg[Re(CO)_5]_2 \xrightarrow[\text{reflux}]{\text{diglyme}} M[Re(CO)_5]_2 + Hg$$

(M = Zn, Cd)

Exchange takes place between $Hg[Re(CO)_5]_2$ and $Hg[Mn(CO)_5]_2$ in THF giving the complex $HgMnRe(CO)_{10}$ which probably has a linear Re–Hg–Mn skeleton. When $Hg[Re(CO)_5]_2$ and HgX_2 (X = Cl, Br, I) are heated briefly in refluxing acetone, the compounds $XHgRe(CO)_5$ are isolated in nearly quantitative amounts.

A unique binuclear complex which does not contain a direct metal–metal bond results from the reaction of *trans*-$CH_3COCH{=}CHRe(CO)_5$ with $Fe_2(CO)_9$ [29]:



$$CH_3COCH{=}CHRe(CO)_5 + Fe_2(CO)_9 \xrightarrow[40°]{C_6H_6} \underset{\underset{Fe(CO)_4}{\downarrow}}{CH_3COCH{=}CHRe(CO)_5}$$

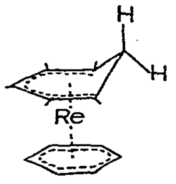
$Fe_2(CO)_9$ is known to react with a variety of monoolefin compounds under similar conditions[176] and it would appear that the rhenium atom in the σ-vinyl derivative has little effect on the reactivity of the double bond.

VI. ARENE COMPLEXES

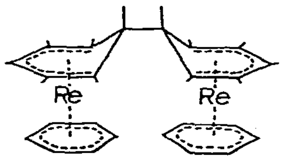
Arenes react with either $ReCl_5$ or $ReCl_3$ to give the cations $[ReAr_2]^+$ (Ar = benzene[177,178], mesitylene[177], hexamethylbenzene[179]) which can be isolated by addition of a suitable large anion (i.e., I_3^-, PF_6^-, $B(C_6H_5)_4^-$) to the reaction mixture.

$$\begin{matrix} ReCl_5 \\ \text{or} \\ ReCl_3 \end{matrix} + Ar \xrightarrow[130°]{Al/AlCl_3} [ReAr_2][AlCl_4^-]$$

Treatment of $[Re(C_6H_6)_2]I_3$ with lithium aluminum hydride in diglyme gives the orange-red π-cyclohexadienyl complex $C_6H_6Re(\pi\text{-}C_6H_7)$ (XXXIX). The bis(hexamethylbenzene) complex $\{Re[C_6(CH_3)_6]_2\}PF_6$ undergoes a similar reduction. However, if the salt $\{Re[C_6(CH_3)_6]_2\}PF_6$ is treated with molten sodium in the absence of solvent the bis(hexamethylbenzene)rhenium dimer of apparent structure (XL) is produced[179]. The



XXXIX



XL

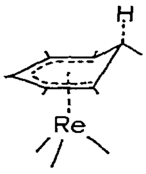
C—C bond holding the two halves of the rhenium molecule together is easily broken by heating in a vacuum to give the monomeric molecule $[(CH_3)_6C_6]_2Re$ which is stable only at extremely low temperatures. ESR measurements indicate this molecule is a free radical having one electron in excess of the favored rare gas configuration. Warming the compound to room temperature causes dimerization with disappearance of the free radicals.

Arenerhenium carbonyl cations can be prepared starting with $Re(CO)_5Cl$ [180,181]

$$Re(CO)_5Cl + Ar \xrightarrow{AlCl_3} [ArRe(CO)_3][AlCl_4] + 2CO$$

(Ar = benzene, toluene, mesitylene, hexamethylbenzene, naphthalene)

As with the bisarene derivatives, the $[C_6(CH_3)_6Re(CO)_3]^+$ cation undergoes hydride ion attack to give complex (XLI). An X-ray crystallographic analysis[182] of (XLI) reveals that the hydrogen atom attached to the ring is in the *exo* position as shown.

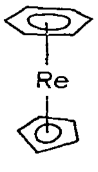


XLI

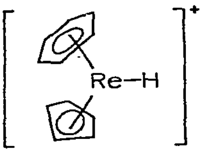
The neutral compound π-benzene-π-cyclopentadienylrhenium(I) (XLII) has been prepared in low yield by the following reaction[183]:

$$ReCl_5 + \text{i-PrMgBr} + CpMgBr + 1{,}3\text{-}C_6H_8 \xrightarrow[\text{ether}]{\text{UV}} C_6H_6ReCp$$

This complex dissolves in aqueous acids forming the cation $[C_6H_6ReHCp]^+$ (XLIII) in which the hydrogen ion, as shown by NMR measurements, is attached to the rhenium atom.



XLII



XLIII

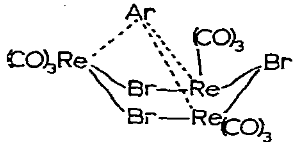
Treatment of C_6H_6ReCp with acetyl chloride in the presence of aluminum bromide results in a mixture of products with the acetyl group either on the benzene or cyclopentadienyl ring.

$$2C_6H_6ReCp + 2AcCl_3 \xrightarrow[CS_2]{AlBr_3} AcC_6H_5ReCp + PhReC_5H_4Ac + 2HCl$$

Bromopentacarbonylrhenium(I) reacts with methyl substituted benzenes (Ar) to form complexes of the stoichiometry $[Re(CO)_3Br]_3 \cdot Ar$ [119].

$$3Re(CO)_5Br + Ar \xrightarrow[130^\circ]{\text{petr. ether}} [Re(CO)_3Br]_3 \cdot Ar + 6CO$$

The proposed structure (XLIV), based on infrared and chemical evidence, allows each rhenium atom to obtain an inert gas configuration without resorting to metal–metal bonds.



XLIV

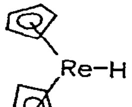
Note added in proof. Another possible structure for these complexes is the ionic formulation $[ArRe(CO)_3][Re_2(CO)_6Br_3]$ The anion would have the configuration shown by structure (X).

The arene ligand is considered to be bound to all three rhenium atoms in the cluster, per se, rather than to an individual metal atom.

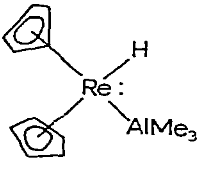
VII. π-CYCLOPENTADIENYL AND BORON CONTAINING COMPLEXES

A. Di-π-cyclopentadienylrhenium hydride

Pentachlororhenium reacts with sodium cyclopentadienide to yield dicyclopentadienylrhenium hydride[184–186]. The presence of the hydride ligand has been confirmed by the appearance of a highfield NMR signal[184,186,187]. The bent structure (XLV) is assigned to the molecule. (XLV) is consistent with IR studies[188], and molecular orbital calculations of such structures which predicts non-bonding pairs between the rings[189].



XLV



XLVI

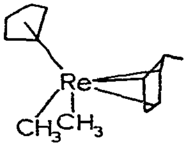
The presence of non-bonding pairs in spatially directed orbitals is consistent with the reactivity of Cp_2ReH. The molecule is basic and readily protonates to yield $[Cp_2ReH_2]^+$ [184,190] In addition, adducts formulated as (XLVI) are formed with BCl_3, BF_3 [191] and $AlMe_3$ [192].

The hydride also reacts with halogens[193]. These dihalides are reduced to the parent hydride by lithium aluminum hydride.

$$Cp_2ReH + X_2 \xrightarrow{CHCl_3} [Cp_2ReX_2]^+$$

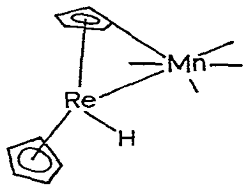
$(X = Cl, Br, I)$

The hydride reacts with n-butyllithium to produce a dilithiated derivative which reacts with D_2O and $HgCl_2$ to yield complexes with a deuterium or HgCl respectively on each ring[194]. The dilithiated product gives a molecule of the stoichiometry $Re(C_{13}H_{19})$ when treated with an excess of methyl iodide[194]. An X-ray crystallographic study of this molecule confirmed the stoichiometry $(C_5H_5)(C_5H_5CH_3)Re(CH_3)_2$ and the molecular structure (XLVII)[195].



XLVII

The donor properties of Cp_2ReH and related molecules have been investigated by reactions with $CH_3Mn(CO)_5$ [196]. In refluxing benzene the hydride reacts with $CH_3Mn(CO)_5$ to yield CO, CH_4 and a binuclear Re–Mn species which displays a parent multiplet in its mass spectrum corresponding to $C_{14}H_{10}O_4ReMn$. The NMR and IR of the product confirm the presence of a H atom attached to the rhenium. A crystallographic study of the product obtained from Cp_2MoH_2 and $CH_3Mn(CO)_5$ indicates the probable formulation $(Cp)(H)Re\text{-}\pi\text{-}C_5H_4Mn(CO)_4$ of structure (XLVIII)[196]. The unusual bridging ring system is susceptible to attack by acids.



XLVIII

B. π-Cyclopentadienyl- and π-indenylrhenium tricarbonyl

π-Cyclopentadienylrhenium tricarbonyl results in high yield from the reaction of sodium[197,198] or thallium[197] cyclopentadienide with $Re(CO)_5Cl$. The analogous reaction utilizing indenylsodium gives an 80% yield of π-$C_9H_7Re(CO)_3$ [198]. $CpRe(CO)_3$ has also been obtained from $Re_2(CO)_{10}$ with dicyclopentadiene[187] and $ReCl_5$ with sodium cyclopentadienide[199]. More recently both the cyclopentadienyl and indenyl products have been obtained from organotin compounds[200]

$$C_5H_5SnMe_3 + Re(CO)_5Br \rightarrow C_5H_5Re(CO)_3 + 2CO + BrSnMe_3$$

$$C_9H_7SnMe_3 + Re(CO)_5Br \rightarrow C_9H_7Re(CO)_3 + 2CO + BrSnMe_3$$

Ring substituted products result from similar reactions. Thus, the reaction of lithium pentamethylcyclopentadienide with $Re(CO)_5Cl$ yields $(CH_3)_5C_5Re(CO)_3$ [201], while $NCC_5H_4Re(CO)_3$ results as a colorless crystalline solid, m.p. 90.5–91.5, from $Re(CO)_5Cl$ and potassium cyanocyclopentadienide[202].

Organotin reagents have proved to be useful for isolating substituted π-cyclopentadienyl complexes[200,203]. The reagents with both organosilicon and organotin substituents yield

$$MeC_5H_4SnMe_3 + Re(CO)_5Cl \rightarrow MeC_5H_4Re(CO)_3$$

$$Me_3SiC_5H_4SnMe_3 + Re(CO)_5Br \rightarrow Me_3SiC_5H_4Re(CO)_3$$

$$Me_5Si_2C_5H_4SnMe_3 + Re(CO)_5Br \rightarrow Me_5Si_2C_5H_4Re(CO)_3$$

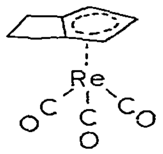
$$Me_3SiCH_2C_5H_4SnMe_3 + Re(CO)_5Br \rightarrow Me_3SiCH_2C_5H_4Re(CO)_3$$

$$(Me_3SnC_5H_4)_2SiMe_2 + Re(CO)_5Br \rightarrow Me_2Si[C_5H_4Re(CO)_3]_2$$

$$(Me_3Si)_2C_5H_3SnMe_3 + Re(CO)_5Br \rightarrow (Me_3Si)_2C_5H_3Re(CO)_3$$

the methylsilyl products exclusively with no trace of the organotin substituted products.

Trimethylenecyclopentadienylrhenium tricarbonyl has been isolated from the reaction of $Re_2(CO)_{10}$ with either 1,3- or 1,5-cyclooctadiene at 250° for 24 h [204]. The mechanism of the olefin isomerization and dehydrogenation is not known. An X-ray analysis has confirmed structure (XLIX).


XLIX

The cyclopentadienyl ring in $CpRe(CO)_3$ is aromatic and undergoes a variety of substitution reactions. Typical Friedel–Crafts conditions give the acetyl and benzoyl derivatives in about 50% yield[198,205]. A competitive Friedel–Crafts acetylation has established that $CpRe(CO)_3$ is less reactive than Cp_2Fe, $CpMn(CO)_3$ or C_6H_6 [206]. A sulfonic acid derivative has been reported from sulfonation in acetic anhydride–sulfuric acid solution and chloromercuri derivatives from alcoholic mercuric acetate and halide ion[207].

Organolithium reagents such as MeLi, BuLi and PhLi react with $CpRe(CO)_3$ to either lithiate the ring or attack the carbonyl carbon atoms. Reaction in THF at a temperature of –70° to –40° yields the ring lithiated product which will undergo a variety of subsequent reactions. Accordingly, reaction of $LiC_5H_4Re(CO)_3$ with CO_2 followed by hydrolysis yields the expected acid derivative[208]. The acid can be converted to the corresponding acid chloride with $SOCl_2$ and to its methyl ester. The acid chloride, $ClCOC_5H_4Re(CO)_3$, reacts with NaN_3 in acetone to give $N_3COC_5H_4Re(CO)_3$ [209]. This azide derivative undergoes the Curtius rearrangement in benzene–heptane and base hydrolysis of the resulting isocyanate gives 17% of the corresponding amine $NH_2C_5H_4Re(CO)_3$.

Tributylborate reacts with $LiC_5H_4Re(CO)_3$ to yield a boronic acid derivative[210]. This derivative gives $ClHgC_5H_4Re(CO)_3$ with aqueous $HgCl_2$. The chloromercuri derivative has also been obtained in 66% yield from $LiC_5H_4Re(CO)_3$ with $HgCl_2$ in THF followed by an aqueous treatment[211].

$ClHgC_5H_4Re(CO)_3$ reacts with I_2 [211] or CuX_2 ($X = Cl, Br$)[210] to give $XC_5H_4Re(CO)_3$ derivatives. The iodo derivative with copper powder at 150° yields a coupled product[211].

$$IC_5H_4Re(CO)_3 \xrightarrow[150^\circ]{Cu} CuI_2 + [C_5H_4Re(CO)_3]_2$$

If organolithium reagents and $CpRe(CO)_3$ are allowed to react in diethyl ether at approximately –30° nucleophilic attack occurs at a carbonyl carbon atom[212,213].

$$CpRe(CO)_3 + LiR \rightarrow Li[CpRe(CO)_2COR]$$

$$(R = Me, n\text{-}Bu, Ph)$$

The lithium salt can be protonated or alkylated to yield neutral carbene complexes $CpRe(CO)_2C(OR)R$ [212].

The nitrosyl complex $[CpRe(CO)_2NO]^+$ has been reported from the following reactions[214,215]:

$$CpRe(CO)_3 + [NO_2]BF_4 \xrightarrow{CH_3NO_2} [CpRe(CO)_2NO]BF_4 + CO_2.$$

$$CpRe(CO)_3 + NOHSO_4 + NH_4PF_6 \xrightarrow{CH_2Cl_2} [CpRe(CO)_2NO]PF_6 + CO + NH_4HSO_4$$

The NO stretching vibration is observed at 1815 cm^{-1} [215] as compared to 1803 cm^{-1} for $Re_2(CO)_4(NO)_2Cl_4$ [89]. As observed for other cationic complexes, the CO groups in the nitrosyl complex are susceptible to nucleophilic attack by methoxide ion[214].

$$[\mathrm{CpRe(CO)_2NO}]^+ \xrightarrow[\mathrm{CN^-}]{\mathrm{MeOH}} \mathrm{CpRe(CO)(NO)CO_2CH_3} + \mathrm{HCN}$$

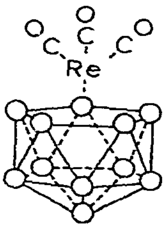
With $NaBH_4$ the cationic complex yields a primary alcohol derivative.

$$\mathrm{CpRe(CO)_2NO} \xrightarrow{\mathrm{NaBH_4}} \mathrm{CpRe(CO)(NO)CH_2OH}$$

Antimony pentachloride reacts with $CpRe(CO)_3$ to yield a yellow unstable salt $[CpRe(CO)_3Cl]SbCl_6$ [158]. Bromine in carbon tetrachloride, however, ruptures the Re–Cp bond and gives pentabromocyclopentane[216]. If the bromination is performed in trifluoroacetic acid a red product, $CpRe(CO)_3Br_2$, of uncertain structure results.

C. Boron containing complexes

The bonding orbitals in the open face of the dicarbollide ion $[B_9H_{11}C_2]^{2-}$ approximate those of the cyclopentadienide ion. Accordingly $[B_9H_{11}C_2]^{2-}$ reacts with $Re(CO)_5Br$ to form a π-complex in which the $Re(CO)_3$ group completes the icosahedron[217]. An X-ray diffraction study has confirmed the structure as (L)[218].

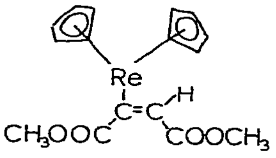


L

The few remaining boron hydride derivatives will be discussed here even though they are not isoelectronic with $CpRe(CO)_3$. The reaction of $P(n\text{-}Bu)_4[Re(CO)_5]$ with diborane yields $[H_3BRe(CO)_5]^-$ and $[(H_3B)_2Re(CO)_5]^-$ as red-orange crystals. These complexes are thought to contain boron–rhenium dative bonds[219]. Octahedral structures of the type $XRe(CO)_5$ ($X = BH_2$, $BH_2{-}HBH_3$) are assigned. Chloro and bromo derivatives of B_5H_9 undergo metatheses reactions with $NaRe(CO)_5$ to yield $2\text{-}[Re(CO)_5]B_5H_8$ [220]. A structure involving a rhenium–boron sigma bond is suggested on the basis of spectral evidence.

VIII. ACETYLENE COMPLEXES

Di-π-cyclopentadienylrhenium hydride reacts rapidly with dimethylacetylene dicarboxylate and methyl propiolate to yield a substituted dimethylmaleate, (LI), and acrylate respectively[221]. From NMR data it is suggested that the initial addition is *cis*. The *cis* dimethylmaleate product is transformed to the corresponding *trans* in the presence of platinum. Upon hydrogenation (LI) yields a complex formulated as $Cp(C_5H_7)Re[CH_3O_2CC(H)CO_2CH_3]$ in which one of the cyclopentadienyl groups has been transformed into an allyl group[221].



LI

Very stable diamagnetic acetylene complexes have been obtained from the trimeric species $[Re(Cl_3)]_3$ and $[(PPh_3)ReCl_3]_3$ [222]. IR evidence suggests that the acetylenes are

$$RCCH + [ReCl_3]_3 \rightarrow ReCl(RCCH)_2$$

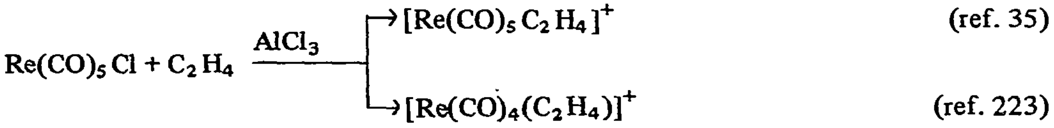
$$RCCH + [PPh_3ReCl_3]_3 \rightarrow ReCl(PPh_3)(RCCH)_2$$

$$(R = Ph, H, CMe_2OH)$$

attached to the metal via two Re–C σ bonds.

IX. OLEFIN COMPLEXES

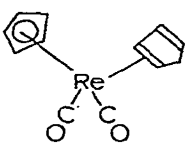
Cationic rhenium olefin complexes have been reported from the reaction of $Re(CO)_5Cl$ with ethylene in the presence of aluminum chloride. The NMR spectra show one resonance



$$Re(CO)_5Cl + C_2H_4 \xrightarrow{AlCl_3} \begin{cases} [Re(CO)_5C_2H_4]^+ & \text{(ref. 35)} \\ [Re(CO)_4(C_2H_4)]^+ & \text{(ref. 223)} \end{cases}$$

at τ 4.92 ($[Re(CO)_5C_2H_4]^+$) and τ 6.6 for ($[Re(CO)_4(C_2H_4)]^+$). For comparison the NMR spectrum of *cis*-$[p\text{-}MePhNH_2(C_2H_4)PtCl_2]$ displays a triplet pattern centered at τ 6.18 [224].

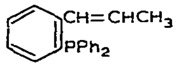
The very stable olefin complex π-cyclopentadienyl(cyclopentadiene)dicarbonylrhenium(I) results when Cp_2ReH is carbonylated at elevated pressures and temperatures[187,190]. The favored structure (LII) is analogous to numerous manganese complexes of the type



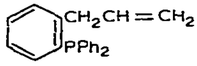
LII

$CpMn(CO)_2$olefin. (LII) absorbs one mole of hydrogen upon catalytic hydrogenation to yield π-cyclopentadienyl(cyclopentene)dicarbonylrhenium(I).

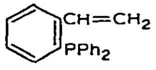
The olefin complexes $Re_2(CO)_2(NO)_2(C_8H_{14})Cl_4$ [91] have been discussed in section IV-A2. Potentially bidentate ligands containing both a phosphorus donor and an olefin yield rhenium olefin complexes. The ligands *cis*-PP, AP and SP react with $Re(CO)_5X$ (X = Cl, Br, I) to yield $Re(CO)_3LX$ in which the ligands are chelating and bidentate[225]. The IR



cis-PP



AP

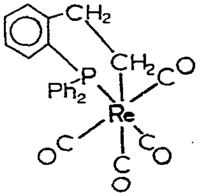


SP

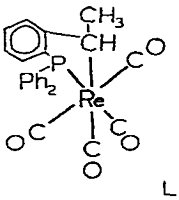
band associated with the C=C stretching motion which appears at approximately 1640 cm^{-1} in the free ligands shifts upon coordination and cannot be located in these complexes.

The phosphine–olefin complexes undergo carbonylation in the presence of $AlCl_3$ to yield $[Re(CO)_4L]^+$ [225]. The olefin portion of the ligand remains coordinated and a band assigned to ν(C=C) is observable in the 1480–1580 cm^{-1} range.

The ligand *o*-styryldiphenylphosphine, SP, reacts with $HRe(CO)_5$ to yield a Re–C σ-bonded complex (LIII)[226]. Reaction of (LIII) with $[Ph_3C]BF_4$ results in hydride abstraction and the formation of $[Re(CO)_4(SP)]^+$ [226], identical to that obtained from the carbonylation of $Re(CO)_3SPX$ [225]. Reduction of $[Re(CO)_4SP]^+$ with $NaBH_4$ yields (LIV)[226].



LIII



LIV

The reactions of $(ReCl_3)_3$ and $(PPh_3ReCl_3)_3$ with dicyclopentadiene have been reported to yield the olefin complexes $ReCl_2(C_{10}H_{12})_2$ and $ReCl(PPh_3)(C_{10}H_{12})$ [222]. These complexes have not been characterized.

X. ALLYL COMPLEXES

The organotin reagent σ-allylMe_3Sn transfers its allyl group to rhenium under mild conditions[200]:

$$\sigma\text{-allyl}(CH_3)_3Sn + Re(CO)_5X \rightarrow \pi\text{-allyl}Re(CO)_4 + (CH_3)_3SnX$$

(X = Cl, Br; allyl = CH_2CHCH_2, $CH_2CHC(H)(CH_3)$, $CH_3CHCHCH_2$, $CH_2C(CH_3)CH_2$, $C_6H_5CHCHCH_2$, $CH_2CHCH(C_6H_5)$)

It is suggested that the reaction takes place via a Re–olefin intermediate rather than a σ-bonded Re–C intermediate.

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