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The chemistry of group-VIb metal carbonyls

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ABSTRACT

The special interest attached to the chemistry of metal carbonyls arises from several causes. While quite distinct from the metal carbonyls in the organometallic compounds, they differ in physical properties (e.g., their volatility) from all other compounds of the transition metals. Chemically, they constitute a group of compounds in which the formal valency of the metal atoms is zero, and in this respect (apart, perhaps, from the ammoniates of the alkali metals) they are comparable only with the recently discovered compounds. As a class, the carbonyls are reactive compounds, and a number of new types of inorganic compounds have been discovered. In the concepts for new products, performance, product safety, and product economy criteria are equally important. They are taken into account already when the raw material base for a new industrial product development is defined. Since the discovery of nickel carbonyl by Mond and Langer in 1888, the carbonyls of the iron group and of chromium, molybdenum and tungsten have found important technical applications, e.g., in the Mond nickel process, and for the preparation of the metals in a state of subdivision and of purity suitable for powder metallurgy, for catalysts, etc. The reaction mechanism of the processes developed for producing the carbonyls technically has only recently received its interpretations. Within the space of review it is necessary to limit discussion to a few topics. Particular stress has accordingly laid upon (a) the chemical bonding in metal carbonyls, (b) importance of IR and NMR spectroscopy in characterization of metal carbonyls, (c) substitution reactions of G-VIb metal carbonyls, (d) kinetics and mechanism of substitution reactions in metal carbonyls, (e) substituted complexes of G-VIb metal carbonyl, (f) chelate complexes of G-VIb metal carbonyls, (g) uses of G-VIb metal carbonyl complexes and (h) studies done on G-VIb metal carbonyls.

1. Introduction

Binary metal carbonyl compounds that consist only of a metal and carbon monoxide (CO) ligands are usually prepared by direct reaction of the powder of a highly reactive metal and carbon monoxide, or by the reduction of a metal salt to zero valance followed by reaction with high-pressure carbon monoxide. However, tetracarbonyl nickel first discovered at the end of the 19th century, forms by the reaction of nickel metal and carbon monoxide under atmospheric pressure and at room temperature. The preparation of other metal carbonyl compounds, on the other hand, requires high temperatures and high pressures.

Carbonyl groups are the functional group consisting of a carbon atom bonded to an oxygen atom through a double bond. In certain other carbonyl compounds, where carbon monoxide functions as a ligand in some inorganic and organometallic complexes, carbon is bonded to Oxygen through a triple bond (C≡O).

In metal carbonyl a transition metal is bonded to CO. Elements from d-block of the periodic table are usually referred to as transition metals as they contain an incomplete d sub-shell. CO forms bonds with metal ions through π-backbonding. Metal carbonyls are most of the times non-polar and electrically neutral compounds and demonstrates physical properties of organic compounds. The general formula of metal carbonyls is $M_x(CO)_y$. These complexes may be homoleptic, that is containing only CO ligands, such as nickel carbonyl ($Ni(CO)_4$), but more commonly metal carbonyls contain a mix of ligands, such as $Re(CO)_3$(2,2'-bipyridine)Cl. Carbon monoxide is an important building block for the synthesis of many compounds, for example hydro formylation, and metal carbonyl catalysts are central to its utilization. Metal carbonyls are toxic, in part because of their ability to carbonylate hemoglobin to give carboxy hemoglobin, which will not bind O_2 [1]. Most of metal carbonyls are solid at ordinary temperatures, but nickel carbonyl, iron pentacarbonyl and ruthenium pantacarbonyls are liquid, and cobalt hydrocarbonyl is gas. Most metal carbonyl reacts vigorously with oxygen and oxidizing substances, and some ignite spontaneously. Metal carbonyls include solubility in only organic solvent but have poor solubility with water, highly toxic nature, volatile solid or liquid appearance at room temperature.

1.1. Bonding in metal carbonyls

A simple molecular orbital (MO) diagram for CO is shown below (Figure 1). The highest occupied molecular orbital (HOMO) is indicated by the pair of electrons. This is the 5σ lone pair orbital mainly centered on the carbon and weakly anti bonding with respect to the C-O bond.

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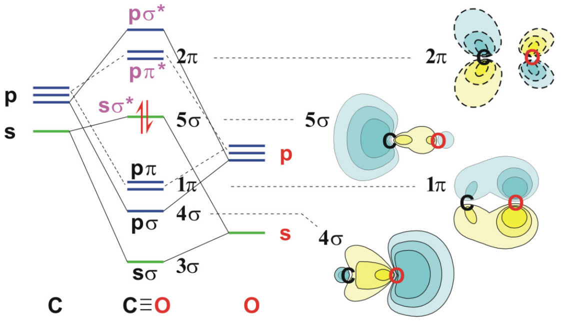


Figure 1. Molecular orbital diagram of CO.

Figure 2. π*-Acceptor orbitals on carbonyl.

The weak C-O antibonding nature of this MO, however, is clearly seen in the experimental data presented below. The LUMO is strongly π* antibonding and is low enough in energy to act as a good acceptor orbital for interacting with filled *d*-orbitals on metals.

CO forms bonds with metal ions through π-back bonding. As a result of π-back bonding, the transition metal attains nearer inert gas electron configuration. CO contains lone pairs of electrons on carbon atom and forms sigma bond to the metal. The metal atom inturn donates electrons from its valence *d*-shell to π orbitals of CO (Figure 2) and metal atom attains inert gas configuration due to this donation of valence electrons (Figure 3).

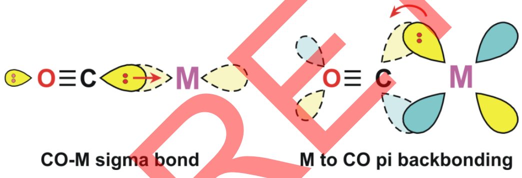


Figure 3. π-Back bonding between metal and CO group.

For an example, in chromium hexacarbonyl [$Cr(CO)_6$], elemental chromium contains six valence electrons hence combines with six CO molecules and attains isoelectronic configuration with nearer inert gas krypton (Kr).

1.2. Bonding modes in clusters

The carbonyl ligand engages in three types of bonding modes in metal carbonyl cluster chemistry [1,2]. Most frequently, CO binds in the familiar terminal mode, but CO is often bridges between two (μ_2) or three (μ_3) metals (Figure 4). Much less common are bonding modes in which both C and O bond to the metal, e. g. μ_3-η^2.

The increased π-bonding due to back-donation from multiple metal centers results in further weakening of the C-O bond.

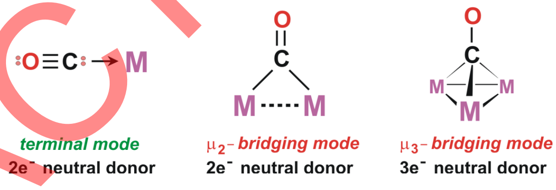
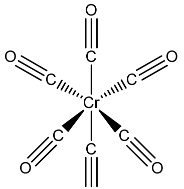


Figure 4. Standard CO bonding modes in metal carbonyl clusters.

1.3. Chromium hexacarbonyl

Chromium carbonyl, also known as chromium hexacarbonyl, is the chemical compound with the formula $Cr(CO)_6$ (Scheme 1). At room temperature the solid is stable to air, although it does have a high vapor pressure and sublimes readily. $Cr(CO)_6$ is zero valent, meaning that Cr has a formal charge of zero, and it is called a homoleptic complex, which means that all the ligands are the same.



Scheme 1

1.3.1. Structure

The complex is octahedral with Cr-C and C-O distances of 1.92 and 1.17 Å, respectively (Scheme 1) [3].

1.3.2. Properties

Chromium hexacarbonyl is white crystals or powder. It is white crystalline or granular solid which sublimes at room temperature and burns with a luminous flame.

Chromium hexacarbonyl is insoluble in water and alcohol but soluble in most of organic solvents. Chromium hexacarbonyl decomposes violently at 210 °C. Chromium hexacarbonyl is decomposed by chlorine and fuming nitric acid, Chromium hexacarbonyl is incompatible with oxidizing agents. Flash Point for chromium hexacarbonyl is 210 °C, however, it is probably combustible [4].

1.3.3. Preparation

The chromium hexacarbonyls can be prepared by any one of the following methods. Chromium hexacarbonyl has been prepared by reacting chromic chloride with phenyl magnesium bromide (Grignard reagent) and carbon monoxide in an ethereal solution. A carbon monoxide pressure of one atmosphere or somewhat higher is required. This process requires a large amount of phenyl magnesium bromide (Grignard reagent) therefore is impractical for technical preparation of chromium hexacarbonyl.

Brimm *et al*. found a alternate method for preparation of Chromium hexacarbonyls by reacting anhydrous chromium chloride with carbon monoxide in the presence of an aromatic solvent compound, a Friedel-Craft catalyst $AlCl_3$ and Al as reducing agent under pressure at 140 °C temperature [5] (Scheme 2).

$$CrCl_3 + Al + 6CO \xrightarrow[C_6H_6]{AlCl_3} Cr(CO)_6 + AlCl_3$$

Scheme 2

1.3.4. Applications in inorganic and organometallic chemistry

Chromium hexacarbonyl is useful in serving as a decomposable material in the production of metallic coatings, such as for mirrors, as a catalyst and as a chemical intermediate. It is used as a catalyst for polymerization and isomerization of olefins. When heated or photolyzed in tetrahydrofuran (THF) solution, $Cr(CO)_6$ converts to $Cr(CO)_5$(THF) with loss of one CO ligand. Similarly, heating a solution of $Cr(CO)_6$ in an aromatic solvent results in replacement of three CO ligands (Scheme 3).

$$Cr(CO)_6 + C_6H_5R \longrightarrow Cr(CO)_3(C_6H_5R) + 3CO$$

Scheme 3

Such reactions proceed particularly well with electron-rich arenes such as anisole, either as the neat reagent or using a mixture of THF and dibutyl ether, the latter to increase the boiling point of the mixture. The products adopt a "piano-stool" structure. These species are typically yellow solids, which dissolve well in common organic solvents. The arene can be liberated from the chromium with iodine or by photolysis in air. In general, substituted derivatives of $Cr(CO)_6$ decompose upon exposure to air.

Alkyl and aryl organolithium reagents RLi add to a carbonyl ligand to give anionic acyl complexes [1]. These species react with alkylating agents such as Me_3O^+ to form $(OC)_5Cr{=}C(OMe)R$, an example of a Fischer carbene. If the R group is a vinyl or an aryl group, then the resulting carbene complex can react with an acetylene to form a new benzene ring to which is bonded the chromium tricarbonyl fragment. The two acetylene carbon atoms become part of the new ring, as does a carbon from one of the carbonyl ligands. Also the three carbons from the vinyl carbene become part of the new benzene ring.

1.3.5. Safety and handling

In common with many of the other homoleptic metal carbonyls (e. g. nickel carbonyl and iron carbonyl), chromium hexacarbonyl is toxic and thought to be carcinogenic. Its vapor pressure is relatively high for a metal complex, 1 mm Hg (36 °C) [6]. Safety information for chromium hexacarbonyl is given in Table 1[7].

Table 1. Safety information of chromium hexacarbonyl.

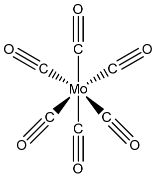
Safety parameter	Safety Data	Explanation
Symbol	 GHS06	Acute toxicity (oral, dermal, inhalation), categories 1,2,3
Signal word	Danger	-
Hazard statement	H301	a. Letter "H" (for "hazard statement"). b. A number '3' for health hazard. c. Two numbers '01' for explosive properties (00-10).
Precautionary statements	P301 + P310	P301 IF SWALLOWED: P310 Immediately call a POISON CENTER or doctor/physician.
Hazard Code	T	For 'Toxic'
Risk Statements	22	Harmful if swallowed

1.4. Molybdenum hexacarbonyl

Molybdenum hexacarbonyl (also called molybdenum carbonyl) is the chemical compound with the formula $Mo(CO)_6$ (Scheme 4). This colorless solid, like its chromium and tungsten analogues, is noteworthy as a volatile, air-stable derivative of a metal in its zero oxidation state.

1.4.1. Structure

$Mo(CO)_6$ adopts an octahedral geometry consisting of six rod-like CO ligands radiating from the central Mo atom (Scheme 4). A recurring minor debate in some chemical circles concerns the definition of an "organometallic" compound. Usually, organometallic indicates the presence of a metal directly bonded via a M-C bond to an organic fragment, which must in turn have a C-H bond. By this strict definition, $Mo(CO)_6$ is not organometallic.



Scheme 4

1.4.2. Properties

$Mo(CO)_6$ is a white crystalline solid; melts at 150 °C; insoluble in water, soluble in most organic solvents.

1.4.3. Preparation

$Mo(CO)_6$ is prepared by the reduction of molybdenum chlorides or oxides under a pressure of carbon monoxide, although it would be unusual to prepare this inexpensive compound in the laboratory. The compound is somewhat air-stable and sparingly soluble in nonpolar organic solvents. Molybdenum hexachloride is reacted with carbon monoxide under pressure in the presence of zinc or aluminum powder in anhydrous ether at 150 °C [8].

1.4.4. Applications in inorganic and organometallic synthesis

Molybdenum hexacarbonyl is widely used in electron beam-induced deposition technique. It is easily vaporized and decomposed by the electron beam providing a convenient source of molybdenum atoms [9] Mo(CO)$_6$ is also a popular reagent in organometallic synthesis [10] because one or more CO ligands can be displaced by other donor ligands [11]. For example, Mo(CO)$_6$ reacts with 2,2'-bipyridine to afford Mo(CO)$_4$(bipy). UV-photolysis of a THF solution of Mo(CO)$_6$ gives Mo(CO)$_5$(THF). Many metal carbonyls are similarly photo-activatable.

Mo(CO)$_6$, [Mo(CO)$_3$(MeCN)$_3$], and related derivatives are employed as catalysts in organic synthesis. For example, these catalysts can be used for alkyne metathesis and the Pauson-Khand reaction.

1.4.5. Safety and handling

Like all metal carbonyls, Mo(CO)$_6$ is dangerous source of volatile metal as well as CO. It diffuses readily into plastic stoppers [12-14]. Safety Information for molybdenum hexacarbonyl is given in Table 2.

1.5. Tungsten hexacarbonyl

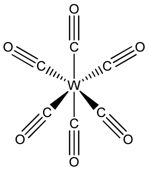
Tungsten hexacarbonyl (also called tungsten carbonyl) is the chemical compound with the formula W(CO)$_6$ (Scheme 5). This complex gave rise to the first example of a dihydrogen complex [15].

1.5.1. Structure

W(CO)$_6$ adopts an octahedral geometry consisting of six rod-like CO ligands radiating from the central W atom with dipole moment 0.0 D (Scheme 5).

Table 2. Safety information of molybdenum hexacarbonyl.

Safety parameter	Safety Data	Explanation
Symbol	 GHS06	Acute toxicity (oral, dermal, inhalation), categories 1,2,3
Signal word	Danger	-
Hazard statement	H300-H310-H330	a. Letter "H" (for "hazard statement"). b. A number '3' for health hazard. c. Two numbers '01' for explosive properties (codes from 00-10). d. Two numbers '30' for flammability (codes from 20 to 30).
Precautionary statements	P260-P264-P280-P284-P301 + P310-P302 + P350	P260 Do not breathe dust/fume/gas/mist/vapours/spray. P264 Wash hands thoroughly after handling. P280 Wear protective gloves/protective clothing/eye protection/face protection. P284 Wear respiratory protection. P301 IF SWALLOWED: P310 Immediately call a POISON CENTER or doctor/physician. P302 IF ON SKIN: P350 Gently wash with plenty of soap and water.
Hazard Code	T+	For 'Very Toxic'
Risk Statements	26/27/28	26: Very Toxic by inhalation 27: Very Toxic in contact with skin 28: Very Toxic if swallowed



Scheme 5

1.5.2. Properties

This colorless compound, like its chromium and molybdenum analogs, is noteworthy as a volatile, air-stable derivative of tungsten in its zero oxidation state. W(CO)$_6$ is a white crystalline solid; melts at 170 ^{o}C; sublimes; boil at 175 ^{o}C. It is insoluble in water and alcohol; soluble in fuming nitric acid and most organic solvents.

1.5.3. Preparation

W(CO)$_6$ is prepared by the reduction of WCl$_6$ under a pressure of carbon monoxide. It would be rare to prepare this inexpensive compound in the laboratory because the apparatus is expensive and the compound can be purchased cheaply. Dallas T. Hurd prepared tungsten hexacarbonyl when tungsten hexachloride is reacted with carbon monoxide under pressure in the presence of zinc or aluminum powder in anhydrous ether at 100 ^{o}C [8].

1.5.4. Applications in inorganic and organometallic synthesis

All reactions of W(CO)$_6$ commence with displacement of some CO ligands in W(CO)$_6$. W(CO)$_6$ behaves similarly to the Mo(CO)$_6$ but tends to form compounds that are kinetically more robust. One derivative is the dihydrogen complex W(CO)$_3$[P(C$_6$H$_{11}$)$_3$]$_2$(H$_2$) reported in 1982 by Kubas [15] Three of these CO ligands can be displaced by acetonitrile [16]. W(CO)$_6$ has been used to desulfurize organosulfur compounds and as a precursor to catalysts for alkene metathesis.

1.5.5. Safety and handling

Like all metal carbonyls, W(CO)$_6$ is dangerous source of volatile metal as well as CO [9,17]. Safety Information for Tungsten hexacarbonyl is given in Table 3.

1.6. Importance of IR spectroscopy in characterizing metal carbonyls

The most important technique for characterizing metal carbonyls is infra-red spectroscopy. The C-O vibration, typically called ν_{CO}, occurs at 2143 cm^{-1} for CO gas. The positions of the ν_{CO} band(s) for the metal carbonyls are inversely correlated with the strength of the π-bonding between the metal and the carbon.

In addition to their frequency, the number of the ν_{CO} bands is diagnostic of structure of the complex. Octahedral complexes, e.g. Cr(CO)$_6$, exhibits only a single ν_{CO} band in its IR spectrum. Spectra for complexes of lower symmetry are more complex. For example, the IR spectrum of Fe$_2$(CO)$_9$displays CO bands at 2082, 2019 and 1829 cm^{-1}.

In cluster carbonyls, ν_{CO} is a sensitive probe for the CO coordination geometry. For bridging (μ_2) ligands ν_{CO} is usually shifted by 100-200 cm^{-1} to lower wavenumbers compared to the signatures of μ_1-CO. Bands for face capping (μ_3) CO ligands appear at even lower energies. Typical values for IR bands in cluster carbonyls are given in Table 4 [18].

Table 3. Safety information of tungsten hexacarbonyl.

Safety parameter	**Safety Data**	**Explanation**
Symbol	 GHS06	Acute toxicity (oral, dermal, inhalation), categories 1,2,3
Signal word	Danger	
Hazard statement	H301-H311-H331	a. Letter "H" (for "hazard statement"). b. A number '3' for health hazard. c. Two numbers '01' for explosive properties (00-10). d. Two numbers '11' for Acute Toxicity properties (10-13). e. Two numbers '31' for flammability (codes from 20 to 30).
Precautionary statements	P261-P280-P301 + P310-P311	P261 Avoid breathing dust/fume/gas/mist/vapours/spray P280 Wear protective gloves/protective clothing/eye protection/face protection. P301 IF SWALLOWED: P310 Immediately call a POISON CENTER or doctor/physician. P311 Call a POISON CENTER or doctor/physician.
Hazard Code	T	For 'Toxic'
Risk Statements	23/24/25	23: Toxic by inhalation 24: Toxic in contact with skin 25: Toxic if swallowed
Safety Statements	36/37-45	36: Wear suitable protective clothing 37: Wear suitable gloves 45: In case of accident or if you feel unwell, seek medical advice immediately (show label where possible)

Table 4. Typical IR-bands for ν_{CO} in cluster carbonyls.

Compound	**ν_{CO} (cm^{-1})**
CO	2143
$[Ti(CO)_6]^{-2}$	1748
$[V(CO)_6]^-$	1859
$[Cr(CO)_6]$	2000
$[Mn(CO)_6]^+$	2100
$[Fe(CO)_6]^{2+}$	2204
$[Fe(CO)_5]$	2022, 2000

As one goes from a terminal CO-bonding mode to 2-bridging and finally 3-bridging, there is a relatively dramatic drop in the CO stretching frequency seen in the IR. Note that these ranges are typical for "neutral" transition metal complexes with an average amount of electron density on the metal center (Table 5). Bridging carbonyls tend to have weaker and broader IR bands.

Table 5. Detecting effect of electron density on metal.

***d*^{x}**	**Complex**	**ν_{CO}(cm^{-1})**
	Free CO	2143
d^{10}	$[Ag(CO)]^+$	2204
	$[Ni(CO)_4]$	2060
	$[Co(CO)_4]^-$	1890
	$[Fe(CO)_4]^{2-}$	1790
	$[Mn(CO)_6]^+$	2090
d^6	$[Cr(CO)_6]$	2000
	$[V(CO)_6]^-$	1860

As the electron density on a metal center increases, more π-back bonding to the CO ligand(s) takes place. This futher weakens the C-O bond by pumping more electron density into the formally empty carbonyl π* orbital. This increases the M-CO bond strength making it more double-bond-like, i.e., the resonance structure M=C=O assumes more importance.

This can clearly be seen on Table 6 that illustrates the effect of charge and electronegativity on the amount of metal to CO π-back bonding and the CO IR stretching frequency.

Table 6. Detection of ligand donation effects.

Complex	**ν_{CO}(cm^{-1})**
$Mo(CO)_3(PF_3)_3$	2090, 2055
$Mo(CO)_3(PCl_3)_3$	2040, 1991
$Mo(CO)_3\ [P(OMe)_3]_3$	1977, 1888
$Mo(CO)_3(PPh_3)_3$	1934, 1835
$Mo(CO)_3(NCCH_3)_3$	1915, 1783
$Mo(CO)_3$(triamine)$_3$	1898, 1758
$Mo(CO)_3$(pyridine)$_3$	1888, 1746

The ability of the ligands on a metal to donate electron density to the metal center certainly has considerable effect on the absolute amount of electron density on that metal. This, in turn, naturally affects the π CO IR stretching frequencies in metal carbonyl complexes. Ligands that are *trans* to a carbonyl can have a particularly large effect on the ability of the CO ligand to effectively π –back bond to the metal. For example 2 *trans*π-back bonding ligands will partially compete for the same *d*-orbital electron density, weakening each others net M-L π-back bonding (Figure 5).

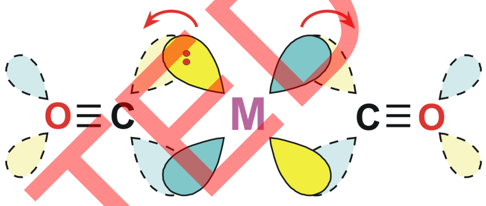


Figure 5. π-Back bonding between metal and CO ligand.

When the *trans* ligand is a π-donating ligand, this can increase the M-CO bond strength (more M=C=O character) by allowing unimpeded metal to CO π-back bonding. Pyridine and amines are not that strong π-donors, but they are even worse π -backbonding ligands. So the CO has virtually no competition for π-back donation.

Based on CO IR stretching frequencies, the following ligands can be ranked from best π-acceptor to worst:

$$NO^+ > CO > PF_3 > RN{\equiv}C > PCl_3 > P(OR)_3 > PR_3 > RC{\equiv}N > NH_3$$

Metal carbonyls have the general formula $Me_x(CO)_y$, and are formed by combination of the metal (Me) with carbon monoxide (CO). Most are solids at ordinary temperatures, but nickel carbonyl, iron pentacarbonyl and ruthenium pentacarbonyl are liquids, and cobalt hydrocarbonyl is a gas. Most metal carbonyls react vigorously with oxygen and oxidizing substances, and some ignite spontaneously.

1.7. Importance of NMR spectroscopy in investigation of metal carbonyl complexes

NMR spectroscopy is useful for investigating complexes containing spin-spin active nuclei (^1H, ^{13}C, ^{31}P and^{19}F etc.). NMR spectroscopy is also useful in confirmation of ligands having P and F atoms. NMR spectroscopy is also useful in differentiating the ligands based on alkyl/aryl groups.

2. Substitution reactions of metal carbonyl complexes

Ligand substitution reactions are essential for the use of transition metal organometallic compounds. Therefore, it is important that we know what factors affect the rates of reaction and why. Much information, both qualitative and quantitative, is available on the reactivity of organometallic compounds [19]. What is needed are more detailed kinetic studies that give information on the mechanisms of ligand substitution, and on what factors contribute to rates of reaction in these systems. Studies on different types of metal carbonyl substituted systems are described here.

$M(CO)_6$ are also a popular reagent in organometallic synthesis [20] because one or more CO ligands can be displaced by other donor ligands [21]. Subasi *et. al*. done substitution of CO ligand by the reaction of $M(CO)_5Br$ with a ligand (L) the products of type $M(CO)_4(L)Br$ formed which confirms that the coming ligand substitute the CO [22]. Photolysis of the allenylidene pentacarbonyl chromium complexes $[(CO)_5Cr=C=C=C(R^1)R^2]$ ($R^1=NMe_2$, NPh_2; $R^2=NMe_2$, OMe, Ph) in THF in the presence of equimolar amounts of XR_3 (XR_3=various phosphanes, $P(OMe)_3$, $AsPh_3$, $SbPh_3$) affords *cis*-allenylidene tetracarbonyl XR_3 complexes, *cis*- $[(CO)_4(XR_3)Cr=C=C=C(R^1)R^2]$ [23]. The interaction between the cavitands, P(III)-phosphocavitands, and the Cr, Mo, W, and Mn carbonyl complexes found possibility of the directed coordination of all or some phosphorus atoms of the cavitand molecules with metals (Figure 6) [24].

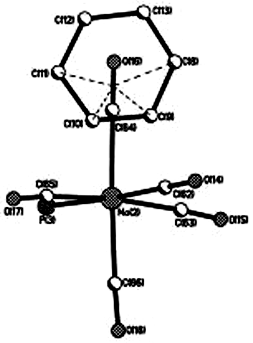


Figure 6. The figure illustrating the formation of the intramolecular CO···Ph contact in phosphocavit and complex of molybdenum hexacarbonyl [24].

Some ligand-ligand substitution reaction also been observed. The reaction of $[M(CO)_4(\eta^2\text{-}C_2H_2)]$ (M=Fe, Os) compounds with $[(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_5]$ proceeds by unexpected substitution of the acetylene ligand by the $W{\equiv}CC_6H_5$ pseudo-alkyne unit and formation of $[MW(\mu\text{-}CC_6H_5)(CO)_6(\eta^5\text{-}C_5H_5)]$ (M=Fe, 1; Os, 2) [25]. The labile complex $W(CO)_5(\eta^2\text{-btmse})$ undergoes replacement of *bis*(trimethyl silyl)ethyne, btmse, by triphenylbismuthine in cyclohexane solution at an observable rate in the temperature range of 35-50 °C yielding almost solely $W(CO)_5(BiPh_3)$ as the final product [26].

2.1. Substitution reactions of metal carbonyls in presence of decarbonylating agents

In organometallic chemistry, Me_3NO is employed as a decarbonylating agent according to the following stoichiometry (Scheme 6).

$$M(CO)_n + Me_3NO + L \longrightarrow M(CO)_{n-1}L + Me_3N + CO_2$$

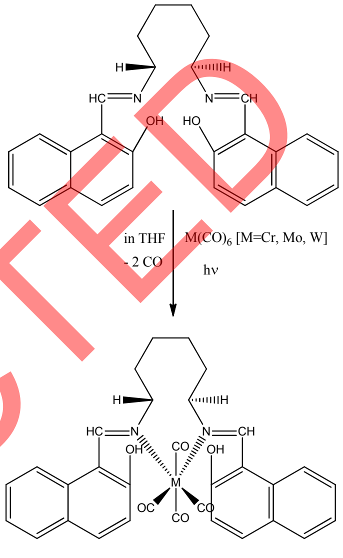
Scheme 6

This reaction is used to decomplex organic ligands from metals, e. g. from $(Diene)Fe(CO)_3$ [27]. It is also used in certain oxidation reactions, e. g. the conversion of alkyl iodides to the aldehyde [28]. Me_3NO induced substitution reactions of $(\eta^5\text{-}C_5H_5)MoMn(CO)_8$ with $P(OMe)_3$ and *t*-BuNC results in facile Mo---Mn bond cleavage products as well as the synthesis of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_4$ $[P(OMe)_3]$ in which $P(OMe)_3$ occupies a site trans to the Mo---Mn bond [29] .

2.2. Photochemically induced substitution reactions of metal carbonyls

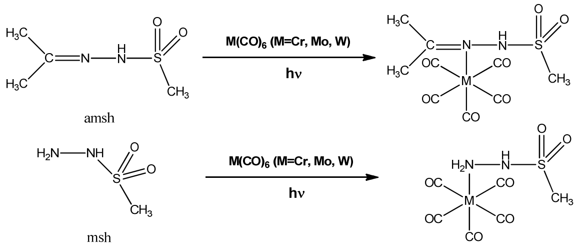
During early 1960's Strohmeier [30] published several papers on photochemical substitution reaction of metal carbonyls with their derivatives. Later additional interest in photolysis of group VI metal carbonyls developed among various scientists [31-37]. Most of these studies have centered around the photolysis of parent hexacarbonyls and the nature of the species $M(CO)_5$ generated in these reactions. The metal carbonyl complexes show photochemical substitution reaction proved earlier [38]. It has long been known that metal carbonyl compounds eliminate a CO group on photolysis in UV [39].

Many metal carbonyls are photo-activatable. The hitherto unknown complexes, $[M(CO)_4(\eta^2\text{-}H_2L)]$, [M=Cr; 1, Mo; 2, W; 3]; have been synthesized by the photochemical reactions of VIB metal carbonyls $[M(CO)_6]$ [M=Cr, Mo, W], with chiral Schiff base *N*,*N*'-*bis*-(2-hydroxynaphthalene-1-carbaldehydene)-(1*R*,2*R*)-(-)-diaminocyclohexane (H_2L) in THF (Scheme 7) [40].



Scheme 7

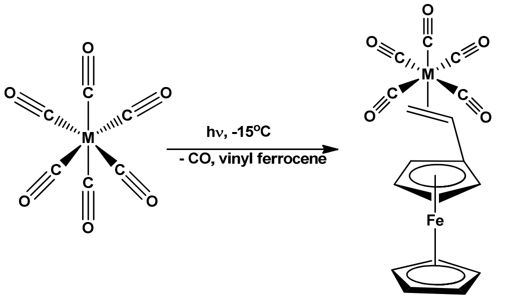
Many complexes based on above hypothesis have been prepared. Photochemical synthesis of metal carbonyl complexes of tetraalkyldiphosphine disulfides, $[M_2(CO)_{10}(\mu\text{-}R_2P(S)P(S)R_2)]$ and $[M(CO)_4(\mu\text{-}R_2P(S)P(S)R_2)]$(M = Mo, W; R = Me) [41] and metal Carbonyl complexes of $M(CO)_6$ (M = Cr, Mo, and W) with acetonemethanesulfonylhydrazone (amsh) and methanesulfonylhydrazone (msh) [42] have been done successfully (Scheme 8).



Scheme 8

Photolytic reaction of the free carbene (L = 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene) with the hexacarbonyls of Cr, Mo and W the corresponding $M(L)(CO)_5$ complexes are generated. Depending on an excess of carbene also the *cis*-$(L)_2Mo(CO)_4$ complex was obtained [43]. Photolysis of $M(CO)_6$ (M=Cr, Mo, W) in the presence of vinyl ferrocene in an *n*-hexane solution at -15 °C yields $M(CO_5)(\eta^2\text{-vinylferrocene})$metal(0) complexes as the sole product (Scheme 9), which could be isolated and characterized by spectroscopic techniques. The complexes were found to be not very stable and their stability increases in the order Cr<Mo<W.

The relatively stable $W(CO)_5(\eta^2$-vinylferrocene) could be isolated as a pure solid [44].



Scheme 9

John K. Ruff and Max Lustig found that the addition of the difluorodithiophosphate anion to a solution of $Cr(CO)_5THF$ in the absence of light produces only trace amounts of the product [45].

2.3. Substitution reactions of metal carbonyls in presence of complexation agents

Complexation agent or ligand is an ion or molecule that binds to a central metal atom to form a coordination complex [46,47]. Although the ligands can directly react with metal carbonyls to form metal carbonyl complexes, but the reaction becomes more easy and gives higher yields when a $M(CO)_x$ transfer reagent is available. Many $M(CO)_x$ transfer reagents are known few of them are discussed below.

2.3.1. M(CO)₅ transfer reagents

The monodentate ligands which easily get replaced with incoming ligands are termed as $M(CO)_5$ transfer reagents.

2.3.1.1. M(CO)₅THF

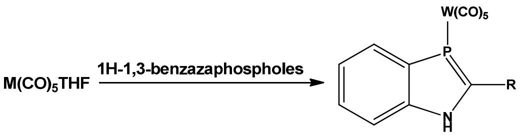
UV-photolysis of a THF solution of $Mo(CO)_6$ gives $Mo(CO)_5(THF)$. A THF solution (150 mL) of $M(CO)_6$ (0.71 mmol) was irradiated with UV light under N_2 stream at room temperature for 2 h to generate the $M(CO)_5THF$ intermediate [48].

The allenylphosphine (L), reacts with $(THF)Cr(CO)_5$ to form the complexes (L)-$Cr(CO)_5$[31]. The complexes $[Et_4N][M(CO)_5SCPh_3]$ (M = Mo, W) were prepared by the reaction of $[Et_4N][SCPh_3]$ with the photogenerated $M(CO)_5THF$ intermediate at ambient temperatures. THF is substituted by reaction of $M(CO)_5THF$ with a monodentate ligand (Scheme 10) [49].

$$M(CO)_6 \xrightarrow[-CO]{\Delta \text{ or } h\nu,\ THF} M(CO)_5THF \xrightarrow{+[Et_4N][SCPh_3]} [Et_4N][M(CO)_5SCPh_3]$$

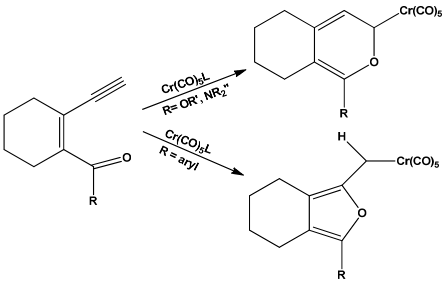
Scheme 10

Reaction of 1*H*-1,3-benzazaphospholes with $M(CO)_5$ (THF) yields the respective´1(P)-metal carbonyl complexes (Scheme 11) [50].



Scheme 11

The reaction of β-ethynyl α,β-unsaturated esters or amides with $Cr(CO)_5(L)$ (L= THF), derived from chromium hexacarbonyl, gives 2-pyranylidene-chromium complexes in good yields (Scheme 12) [51].

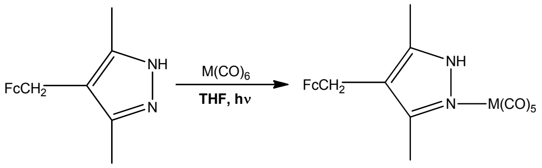


Scheme 12

Subasi *et al.* prepared complexes, $[(\mu\text{-}CO)_2Cr_2(\eta^4\text{-}H_2L)_2]$; $[(\mu\text{-}CO)M_2(CO)_2(\eta^4\text{-}H_2L)_2]$, [M = Mo; W]; $[(\mu\text{-}CO)_2Cr_2(\eta^4\text{-}H_2L')_2]$, and $[(\mu\text{-}CO)M_2(CO)_2(\eta^4\text{-}H_2L')_2]$, [M = Mo; W] have been synthesized by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ (M = Cr, Mo, W) with two oxygen and nitrogen donor Schiff base ligands, *N,N′-bis*(2-hydroxynaphtalin-1-carbaldehydene)-1,2-*bis*(*p*-aminophenoxy)ethane (H_2L) and *N,N′-bis*(2-hydroxynaphtalin-1-carbalde-hydene)-1,4-*bis*(*p*-aminophenoxy)butane (H_2 L′) [52]. They also report the complexes, cis- $[M(CO)_2(\eta^4\text{-}H_2L')]$, [M = Cr; Mo; W] and *cis*- $[M(CO)_2(\eta^4\text{-}H_2L'')]$, [M = Cr; Mo; W] synthesized by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ (M = Cr, Mo, W) with salen type Schiff base ligands, *N,N'-bis*(salicylidene)-1,4-diaminobutane (H_2L') and *N,N'-bis*(2-hydroxy-3-methoxybenzylidene)ethylene diamine (H_2L'') [53].

The reactions of $M(CO)_6$ with ligands using THF as solvent also give same results as found by reactions of $M(CO)_5THF$ and ligand. Reaction of $M(CO)_6$ with 3,5-dimethyl-4-ferrocenylmethylpyrazole under UV irradiation using THF as solvent yields monosubstituted group 6 metalcarbonyl complexes $M(CO)_5L$ (M = Cr, Mo or W; L = 3,5-dimethyl-4-ferrocenylmethylpyrazole) (Scheme 13) [54].

The anionic complexes $[Et_4N]$ $[M(CO)_5SCPh_3]$ (M = Mo, W) were also prepared by direct thermal reaction of equimolar amounts of $[Et_4N]$ $[SCPh_3]$ and the hexacarbonyl parent, $M(CO)_6$, in THF solutions [38].



Scheme 13

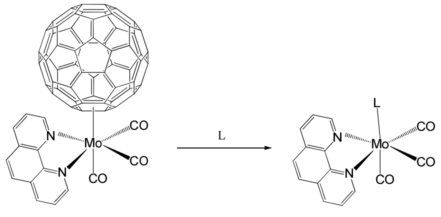
2.3.1.2 M(CO)₅C₆₀

Fullerene (C_{60}) also shows some pathways in preparations of organometallic compounds. The fullerene shows substitution of some ligands like acetonitril and CO or vice versa with some ligands like PPh_3 and PCy_3.

The studies on chemical reactivity of fullerene C_{60} towards fac-$Mo(CO)_3(MeCN)(dppe)$ and $Me(CO)_4(dppe)$ shows that the C_{60} easily replace acetonitril ligands in chlorobenzene at about 80^{o}C to give fac-$Mo(CO)_3(dppe)$ $(\eta^2\text{-}C_{60})$, whereas fullerene C_{60} reacted with $Me(CO)_4(dppe)$ in refluxing chlorobenzene to afford an isomeric mixture of fac- and mer-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ [55].

The Lewis bases (L) triphenylphosphine (PPh_3) and tricyclohexyl phosphine ($P(Cy)_3$) displace 60-fullerene (C_{60})

from the complex *fac*-(η^2-C_{60})(η^2-Phen)$M(CO)_3$ (M = Mo, W) (Phen = 1,10-phenanthroline) (Scheme 14) [56,57].



Scheme 14

2.3.2. $M(CO)_4$ transfer reagents

These reagents have their remarkable importance in synthesis of metal carbonyl complexes with ligands. These $M(CO)_4$ transfer reagents form some complexes which were not easily formed by direct reaction of $M(CO)_6$ with ligands. In this project we use $M(CO)_4$NBD as $M(CO)_4$ transfer reagent and prepared $M(CO)_4L$ type complexes with TDD. If such reaction carried out with $M(CO)_6$ and TDD in equimolar quantities mono-substituted complexes were formed. If we use metalcarbonyls in bimolar quantity, binuclear complexes were formed.

In other preparation we use $M(CO)_4$COD as $M(CO)_4$ transfer reagent with DTTT. DTTT is a monodentate ligand and form $M(CO)_5$DTTT but we were keen to form bisubstituted complexes with DTTT, when we use $M(CO)_4$COD as $M(CO)_4$ transfer reagent, bisubstituted complexes $M(CO)_4(DTTT)_2$ were formed.

The thermal substitution of $Mo(CO)_4$($\eta^{2:2}$-COD) and $Mo(CO)_4$($\eta^{2:2}$-NBD) with, BFEDA gave the same product which was isolated by using the same procedure. Thus, both of $Mo(CO)_4$($\eta^{2:2}$-NBD) and of $Mo(CO)_4$($\eta^{2:2}$-COD) can be used as $Mo(CO)_4$ transfer reagent for the synthesis of $Mo(CO)_4$(BFEDA) [58].

2.3.2.1. $M(CO)_4$ NBD

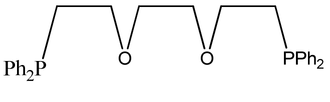
2.3.2.1.1. Preparation of [$M(CO)_4$(nbd)]

R. B. King prepared [$M(CO)_4$(nbd)] by refluxing $M(CO)_6$ and 2,5-norbornadiene ($\eta^{2:2}$-NBD) in 25 mL iso-octane. And yield yellow crystals of the complex on crystallization from n-hexane solution [59-61]. Bennett *et al.* later also prepared [$M(CO)_4$(nbd)] with some other parallel method [62].

2.3.2.1.2. Uses of [$M(CO)_4$(nbd)]as $M(CO)_4$ transfer agent

Reaction of norbornadiene complex $C_7H_8Cr(CO)_4$ with *tris*(dimethylamino)arsine (Tdas) at room temperature gives trans-$(Tdas)_2Cr(CO)_4$ which was isolated as yellow complex. While the reaction of $M(CO)_6$ with Tdas gives monosubstituted complex $(Tdas)Cr(CO)_5$ [63].

[$M(CO)_4$(nbd)] (M=Cr or Mo) react with L^1 ($Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$) (Scheme 15) to give the *trans*- [$Cr(CO)_4(L^1)$] and *cis*- [$Mo(CO)_4(L^1)$] respectively, both of which show coordination of L^1 through the P atoms only, giving 11-membered ring metallocyclic complexes. The crystal structure of [$Mo(CO)_4(L^1)$] confirms the *cis*-geometry of the product [64].



Scheme 15

2.3.2.2. $M(CO)_4$ COD

Fisher and Frohlich prepared [$M(CO)_4$(COD)] by refluxing $M(CO)_6$ and 1,5-cyclooctadiene (COD) in *n*-heptane. Cooling the solution to -35°C yielded yellow crystals of $M(CO)_4$($\eta^{2:2}$-COD) [65]. R. B. King also prepared [$M(CO)_4$(COD)] later [66].

The thermal substitution of 1,5-cyclooctadiene (COD) by *bis*(diphenylphosphino)alkanes , $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (*n* = 1, 2, 3) in $M(CO)_4$($\eta^{2:2}$-COD) complexes (M = Cr, Mo, W), were studied by Kayran *et al.* [67]. The reactions of $Cr(CO)_4$(COD) and $Mo(CO)_4$(NBD) with h5-Cp*Ir(2,5-dimethylthiophene) give modest amounts of the [h6-Cp*Ir(C,S-2,5-Me2T)]$M(CO)_3$ products [68].

2.3.2.3. $M(CO)_4$ (piperidine)$_2$

Mariusz *et al.* prepared $M(CO)_4$(piperidine)$_2$ where (M = Mo, W) by thermal reaction of $Mo(CO)_6$ with piperidine and found *cis*- bonding in $M(CO)_4$(piperidine)$_2$. The two piperidine ligands in this yellow-colored compound are labile, which allows other ligands to be introduced under mild conditions and its dimmers [69].

The reaction of [$Mo(CO)_4$(piperidine)$_2$] with triphenyl phosphine in boiling dichloromethane (b.p. = ~40 °C) gives *cis*-[$Mo(CO)_4(PPh_3)_2$]. This *cis*-complex isomerizes in toluene to *trans*-[$Mo(CO)_4(PPh_3)_2$] [70]. The study on Carbonyl complexes of manganese, rhenium and molybdenum with ethynyliminopyridine ligands found that [$MBr(CO)_5$] reacts with *m*-ethynylphenylamine and pyridine-2-carboxaldehyde in refluxing tetrahydrofuran to give, *fac*- [$MBr(CO)_3$(py-2-CH=N-C_6H_4-*m*-(C≡CH))] (M = Mn, **1a**; Re, **2a**). The same method affords the tetracarbonyl [$Mo(CO)_4${py-2-CH=N-C_6H_4-*m*-(C≡CH)}] (**3a**) starting from [$Mo(CO)_4$(piperidine)$_2$] [71].

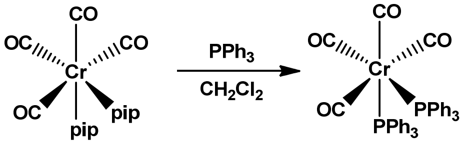
Robert H. Guinn and Regina Gilliland [72] prepared *cis*-[$Mo(CO)_4(PPh_3)_2$] by reaction of *cis*-[$Mo(CO)_4(pip)_2$] with triphenylphosphine (PPh_3) (Scheme 16) in dry CH_2Cl_2 on refluxing at 50 °C for 15 min using previous reference of Allen *et al.* [73].

2.3.2.4. $M(CO)_4$ $(CH_3CN)_2$

It has been reported that nitrile complexes of the group VIB metal carbonyls are prepared by photolytic displacement of carbonyl group to give mono- and disubstituted derivatives [74,75] or by displacement of diglyme in (Diglyme)$Mo(CO)_3$ to give disubstituted derivatives [76]. The photoproduction of metal hexacarbonyl derivatives (M = Cr, Mo, W) in acetonitrile results the formation of species $M(CO)_4(CH_3CN)_2$, $M(CO)_5(CH_3CN)$ and in the cases of Mo and W $M(CO)_3(CH_3CN)_3$ also formed. The metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) are dissolved in acetonitrile resulting colorless solutions when exposed to ultraviolet radiations, they turn bright yellow almost immediately to form the above complexes [77].

Reaction of [$(PPh_2C_5H_4)Cp_3Fe_4(CO)_4$] with $(CO)_4W(CH_3CN)_2$ at ambient temperature affords [$(CO)_4W(PPh_2C_5H_4)Cp_3Fe_4(CO)_4$] as the major product, together with a small amount of [$(CO)_5W(PPh_2C_5H_4)Cp_3Fe_4(CO)_4$] [78].

Isocyanides also forms extensive families of complexes that are related to the metal carbonyls. Typical isocynide ligands are MeNC and t-butylisocyanide (Me_3C-NC). A special case is CF_3NC, an unstable molecule that forms stable complexes whose behavior closely parallels that of the metal carbonyls [79].



Scheme 16

2.3.2.5. M(CO)$_4$(bipy)

2,2'-Bipyridine have been prepared by Smith *et al.* [80]. Darensbourg *et al.* found that these complexes were synthesized by reacting [Mo(CO)$_6$] with excess 2,2'-bipyridine (N-N) ligand in deoxygenated toluene at reflux (Scheme 17). Reaction times for the thermal synthesis of [Mo(CO)$_4$(bipy)] complexes vary between 1.5 to 2.0 hours [81].

$$[Mo(CO)_6] + N\text{-}N \xrightarrow[\text{toluene}]{\Delta} [Mo(CO)_4(N\text{-}N)] + 2\ CO$$

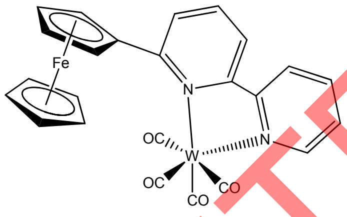
Scheme 17

Later David Manuta *et. al.* synthesize Mo(CO)$_4$(2,2'-bipy) by photolysis of a solution containing the parent hexacarbonyl and 2,2'-bipyridine(N-N) (Scheme 18) [82].

$$[Mo(CO)_6] + N\text{-}N \xrightarrow{h\nu} [Mo(CO)_4(N\text{-}N)] + 2\ CO$$

Scheme 18

Fred Basolo and John McDonald found that the oxidative elimination reactions of M(CO)$_4$L (M = Mo, W; L= 2,2'-bipyridine) with mercuric halides yields M(CO)$_3$L(HgX) and CO using acetone as solvent [83]. 6-Ferrocenyl-2,2′-bipyridine, prepared by the reaction of lithiated ferrocene and bipyridine, reacts with pentacarbonyl [η^2-bis(trimethylsilyl)ethyne] tungsten(0) to form tetracarbonyl(6-ferrocenyl-2,2′-bipyridine)tungsten(0) which was isolated as analytically pure substance (Scheme 19) [84].



Scheme 19

2.3.2.6. M(CO)$_4$(PMe$_3$)$_2$

All metal carbonyls undergo substitution by organophosphorus ligands. For example, the series Mo(CO)$_{6-x}$(PR$_3$)$_x$ is well known for various phosphine ligands for x = 1,2 and 3. PF$_3$ behaves similarly but is remarkable because it readily forms homoleptic analogous of the binary metal carbonyls i. e. Mo(PF$_3$)$_6$.

Air stable and sublimable *bis*(phosphine)metal tetracarbonyls of chromium, molybdenum and tungsten have been prepared by a ligand displacement reaction with the octahydrotriborotetracarbonyl metalate anions (Scheme 20) [85].

$$(CO)_4MB_3H_8^- + 2\ PH_3 \xrightarrow{\text{THF}} (CO)_4M(PH_3)_2 + B_3H_8^-$$

Scheme 20

Klanberg and Mutterties later prepared colorless to faintly yellowish crystalline complexes of type M(CO)$_4$(PH$_3$)$_2$ have been synthesized [86].

Uses: A study on photodissociation of the phosphine-substituted transition metal carbonylcomplexes Cr(CO)$_5$L was performed with time-dependent DFT theory to explore the propensity of the excited molecules to expel their ligands. The influence of the PH$_3$ ligand on the properties of these complexes is compared with the photodissociation behavior of the carbonyl complex Cr(CO)$_6$. All calculations indicate that the excited Cr(CO)$_5$L molecules (L = PH$_3$, PC$_2$H$_5$, and PCH$_3$) prefer dissociation of their phosphorus substituent over that of an CO ligand (Figure 7). This suggests that the photochemical approach may be a viable complement to the ligand exchange and redox methods that are currently employed to demetalate transition metal complexed organophosphorus compounds [87].

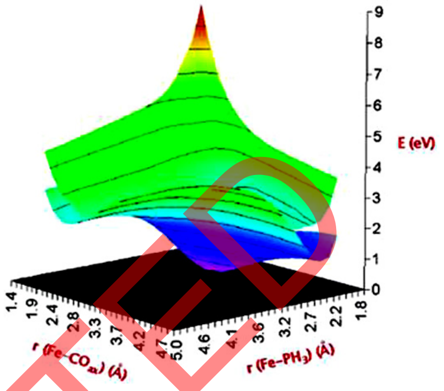


Figure 7. Photodissociation of phosphine-substituted transition metal carbonyl complexes [87].

2.3.3. M(CO)$_3$ transfer reagents

Many ligands are known which act as M(CO)$_3$ transfer reagent. Some of them are discussed here.

2.3.3.1. M(CO)$_3$(acetonitril)

Methyl cyanide (acetonitril) ligands are capable to displace two or three CO molecules from M(CO)$_6$ hence represent properties as M(CO)$_4$ as well as M(CO)$_3$ transfer reagent. But the studies shows that M(CO)$_3$ tranfer properties are more common for acetonitril.

Tate *et al.* find that tri-nitrile derivatives are prepared very conveniently by direct reaction. For instance on refluxing Mo(CO)$_6$ in excess acetonitrile under nitrogen, a near quantitative yield of (CH$_3$CN)$_3$Mo(CO)$_3$ is obtained with evolution of 3 moles of gas in less than 4 hr. It is identical with the compound prepared by Werner and Coffield [76] via a different route. Similarly W(CO)$_6$ give (CH$_3$CN)$_3$W(CO)$_3$ after 40-hr reflux which shows greater air stability. (CH$_3$CN)$_3$Cr(CO)$_3$ also been prepared but it shows extremely sensitivity and less stability. These compounds serves as excellent intermediates in the formation of new compounds not available by other routes [88].

Elschenbroich and Salzer shows that upon refluxing in a solution of acetonitrile, Mo(CO)$_6$ converts to its *tris*(acetonitrile) derivative[Mo(CO)$_3$(MeCN)$_3$]. The resulting air-sensitive compound serves as a source of "Mo(CO)$_3$" [89].

Acrylonitrile complexes (CH$_2$=CHCN)W(CO)$_5$of tungsten carbonyl have been also prepared in which acrilonotril is bonded to tungsten by mean of lone pair of electrons on the nitrogen. The complex is prepared by stirring (CH$_3$CN)W(CO)$_5$ overnight in excess acrylonitrile followed by vacuum evaporation of the displaced acetonitrile and excess acrylonitrile [90].

The reaction of Mo(CO)$_3$(CH$_3$CN)$_3$ and E$_2$Ph$_2$ (E=Se or Te) yields the edge-sharing bioctahedral, metal-metal bonded Mo(I) products [Mo(CO)$_3$(CH$_3$CN)(μ-EPh)]$_2$ [91]. Duterium labeled (fulvene)M(CO)$_3$(M = Cr, Mo) complexes were prepared in high yields by reacting the duterated fulvene ligand with (MeCN)$_3$M(CO)$_3$ [92].

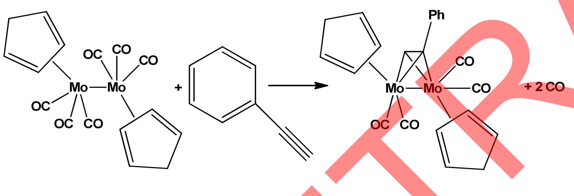
On refluxing $(CH_3CN)_3W(CO)_3$ in 3-hexyne, 2 equivalent CO was evolved and results yellow colored $(CH_3CH_2C{=}CCH_2CH_3)_3W(CO)$ [93]. Thermolysis of $[(Mo(CO)_4(\mu\text{-}DPFB)_2]$ (DPFB = 1,4-*bis* (diphyenylphosphino)-2,5-difluorobenzene) in acetonitrile followed by addition of triphenylphosphine yields *trans*- $[Mo(CO)_4(PPH_3)_2]$ and free DPFB which co-crystallise [94].

2.4. Substitution reactions of cyclopentadienyl and cyclohepatrienyl complexes of $M(CO)_6$

The n-cyclopentadienyl and n-arenes groups are among the most common class of ligand encountered in organotransition metal chemistry. Transition metal complexes with these ligands have been studied extensively and many of which have contributed to the development of areas such as homogenous catalyst, organic synthesis, new materials and biological and medical sciences [95]. A variety of polyolephenic and aromatic hydrocarbons have been shown to react with carbonyls of Group VI metals to afford π-complexes. Compounds of the type $L\text{-}M(CO)_3$ [M = Cr, Mo or W] have been obtained from aromatic hydrocarbons [96-100] and from cycloheptatriene [101,102], 1,3,5-cyclooctatriene [103,104] and even cyclononatetracene [100] In addition to complexes derived from conjugated trienes, metal complexes $L\text{-}M(CO)_4$ involving non conjugating dienes 1,5 cyclooctadiene [105-107] and bicycle-[2.2.1]heptadiene [108,109] have been reported [110].

2.4.1. $M(CO)_4Cp$

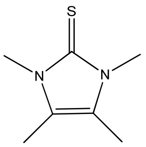
Preparation: $M(CO)_4Cp$ was prepared by thermal substitution reaction of $M(CO)_6$ with cyclopentadiene [111]. The ligand substitution reaction of $M(CO)_4cp$ proceed via CO substitution method (Scheme 21) [112].



Scheme 21

Dicarbonyl(η^5-cyclopentadienyl)iodoiron(II) is widely used and easily prepared precursor for a variety of organometallic iron complexes [113]. McArdle *et al.* and Akita *et al.* have been prepared similar complexes with substituted Cp rings [114,115]. Linkage isomerism in Carbonyl-π-cyclopentadienyl (thiocynato)metal complexes of manganese, chromium, molybdenum, tungsten and rhodium has also been studied by Thomas and Andrew [116].

N-Heterocyclic carbenes (NHC) (Scheme 22) have proved to be excellent ligand in transition metal complexes. Photolysis of $[CpMn(CO)_3]$ in presence of 1,3,4,5-tetramethylimidazoline-2-thione $SC_3N_2Me_4$ produce thione-bridged dinuclear complex $[(CpMn(CO)_2)_2(SC_3N_2Me_4)]$. Mn-S-Mn framework found responsible for dinuclear complexes. Photoreaction of $M(CO)_6$ (M = Mo, W) with $SC_3N_2Me_4$ afforded mononuclear complexes $[M(CO)_5(SC_3N_2Me_4)]$. It was predict that formation of dinuclear complex was somewhat predicted due to presence of Cp ligand [117].



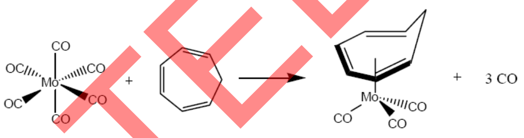
Scheme 22

2.4.2. $M(CO)_3(\eta^6\text{-}C_7H_8)$

Although Cycloheptatriene (C_7H_8) and cycloheptatrienyl (C_7H_7) transition metal carbonyl complexes have been known over six decades. The first cycloheptatriene complex $Mo(CO)_3(C_7H_8)$ was prepared by Wilkinson et al. in 1958 and cycloheptatrienyl complexes shortly after [94].

2.4.2.1. Synthesis of η^6-cycloheptatriene molybdenum tricarbonyl $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$

Moderately air-sensitive organometallic arene complex have been prepared from $Mo(CO)_6$The molecular structure of $(\eta^6\text{-}C_7H_8)Mo(CO)_3$ has been determined by X-ray diffraction [118] and the compound has the structure indicated in Scheme 23. Those of the closely related compounds $(C_6H_6)Cr(CO)_3$ [(benzene) chromium tricarbonyl] [119] and $(Me_6C_6)Cr(CO)_3$ [(hexamethylbenzene) chromium tricarbonyl] [120-122] have also been established in detail and reveal a "piano stool" structure with the arene moiety π-bonded to the metal (Scheme 23).



Scheme 23

Cycloheptatriene in cyclopentadiene/nonane were taken in Schlenk flask or round-bottom flask and add $Mo(CO)_6$ (2. 0 g. 7. 6 mmol) to this flask and heat the contents of the flask carefully to reflux for 2 hours. At the end of the reflux period, cool the reaction mixture to room temperature under a nitrogen gas flow. Red/orange/black $(\eta^6\text{-}C_7H_8)Mo(CO)_3$ solution formed which was crystallized on the alumina cake. Upon washing several times with CH_2Cl_2 solvent $(\eta^6\text{-}C_7H_8)Mo(CO)_3$ crystallize as red solid. The red solid will turn black and decompose if it is exposed to air for only one day [123,124].

The reaction of *tris*(dimethylamino)phosphine(Tdp) and *tris*(dimethylamino)arsine(Tdas) with the $C_7H_8M(CO)_3$ (M = Cr, Mo, W) in hydrocarbon solvents has been investigated. The first step of this reaction appear to be the complete displacement of the coordinated olifin with the legands products with two legands in cis position are found to be unstable & undergo further change by following two processes.

1. Rearrangement of *cis* derivative to *trans* derivative
2. Removal of a ligand by decomposition generated carbon monoxide [125].

The trisubstituted metalcarbonyl complexes containing ligands which coordinate through bicovalent sulfur are reported. Direct reaction of the ligands with cycloheptatrienemolybdenumtricarbonyl $[M(CO)_3(\eta^6\text{-}C_7H_8)]$, complexes of type $Mo(CO)_3L_3$ were prepared where L representing dimethyl sulfide $[(CH_3)_2S]$, diethyl sulfide $[(C_2H_5)_2S]$, thiourea $[(CH_2)_2CS]$, thioacetamide $[CH_2CSNH_2]$ [126].

2.4.3. $M(CO)_3(\eta^6\text{-}C_8H_8)$

Preparation: Winstein *et al.* prepared cyclooctatetraene complexes $(\eta^6\text{-}C_8H_8)Mo(CO)_3$, in which this olefin is bound to a metal by six π-electrons on six carbon atoms [127].

Cyclooctatetraene is displaced from $C_8H_8Ru(CO)_3$ by I_2 or $P(OCH_2)_3CEt$ giving $[Ru(CO)_3I_2]_2$ and *trans*-$[P(OCH_2)_3CEt]_2Ru(CO)_3$, respectively. Mercury(II) chloride, bromide, or thiocyanate also react with $C_8H_8Ru(CO)_3$ to afford the binuclear complexes$[Ru(CO)_3(HgX)X]_2$ (XCl, Br, or SCN), which undergo bridge-splitting reactions with pyridine without breaking the Ru-Hg bond, to give the complexes Ru(CO)$_3$py(HgX)X [128].

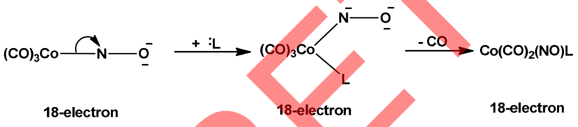
3. Kinetics and mechanism of substitution reactions in metal carbonyls

Ligand substitution reactions are essential for the use of transition metal organometallic compounds as catalysts. Therefore, it is important that we know what factors affect the rates of reactions and why. Much information, both qualitative and quantitative, is available [129] on the reactivity of organometallic compounds. More detailed kinetic study that give information on the mechanism of ligand substitution and the factors contributes to rates of reaction aredescribed here. Fred Basolo found that CO substitution reactions of metal carbonyls proceed via three different systems: (a) compounds where ring slippage seems to be involved in reaction; (b) heterocyclic metal carbonyls, and (c) 17-electron metal complexes [130].

3.1. Ring slipping mechanism

About six decades ago study of CO exchange using ^{14}CO, and of CO substitution with P-ligands on binary metal carbonyls. Since very little work [131] of this type had been done at that time, the observations were often a source of some surprise. For example, Ni(CO)$_4$ was found [132] to exchange CO by a dissociative process, although one might have expected the 4-coordinate complex to readily expend its coordination number to permit a low energy associative pathway for reaction. We discuss and understand this behavior in terms of Tolman's [133] 16- and 18-electron rule. An associative substitution for Ni(CO)$_4$ would require the formation of an unstable 20-electron transition state or active intermediate.

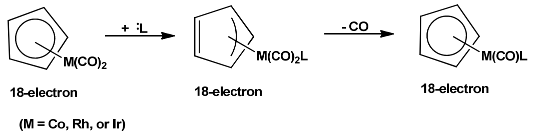
We find [134] that CoNO(CO)$_3$ (Scheme 24) and Fe(NO)$_2$(CO)$_2$, isoelectronic and isostructural with Ni(CO)$_4$, both undergo CO substitution by an associative process. The interpretation given the observation, before the 16-, 18-electron rule and before the bent metal nitrosyl, was that a pair of electrons is localized on the nitrosyl group freeing a low energy metal orbital for nucleophilic attack.



Scheme 24

Such a process that maintains an 18-electron count throughout is much less available for a compound with only CO ligands because N is more electronegative than C and because the nitrosyl ligand is formally present as NO$^+$.

More readily explained after the nitrosyl ligand experience, the observations [135] that the compounds (η^5-C$_5$H$_5$)M(CO)$_2$ (where M = Co, Rh, or Ir) undergo CO substitution by an associative pathway (Scheme 25). Surprisingly, because these compounds are pseudo-isoelectronic with Fe(CO)$_5$ which only very slowly reacts thermally by a dissociative process [131]. More readily interpreted, because after the nitrosyl experience we were prepared to localize a pair of electrons on the cyclopentadienyl ring in order to permit nucleophilic attack of a low energy metal orbital. Some years later it was suggested [136] that the pair of electrons localized on the cyclopentadienyl ring could be formulated as an η^3 allyl-ene system. There isnow X-ray evidence [137] for such a cyclic ligand in the compound (η^5-C$_5$H$_5$)(η^3-C$_5$H$_5$)W(CO)$_2$. This suggests that an η^5→ η^3 → η^{5}associative pathway is involved.



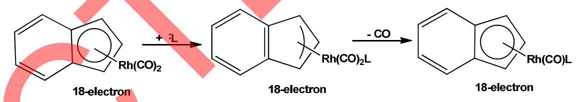
Scheme 25

As expected for a mechanism that requires the flow of electron density from the metal into the cyclic ligand, electron withdrawing substituents (NO$_2$) on the ring enhance rates of CO substitution and electron donating groups (CH$_3$) on the ring retard rates of substitution (Scheme 26).

	(η^5-C$_5$H$_5$)Rh(CO)$_2$	(η^5-C$_5$H$_4$NO$_2$)Rh(CO)$_2$	(η^5-C$_5$(CH$_3$)$_5$)Rh(CO)$_2$
relative rates	1	10^4	10^{-2}

Scheme 26

Furthermore a relative rate increase of 10^8 was observed for (η^5-indenyl)Rh(CO)$_2$ over (η^5-cyclopentadienyl)Rh(CO)$_2$, and this has been termed the indenyl ligand effect [138]. This had been previously observed (Scheme 27) [139] and explained on the basis of the fused six-ring aromaticity in the transition state tending to drive the associative reaction.



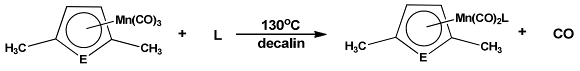
Scheme 27

These studies show it is possible to markedly vary (over 10^{10} times) the rates of ligand substitution of organometallic compounds, and if necessary to fine tune these rates for optimum homogenous catalysis conditions.

3.2. Heterocyclic metal carbonyl mechanism

Although thousands of papers have been published on the synthesis and reactions if η^5-carbocyclic metal carbonyls, much less work has been done with the corresponding η^5-heterocyclic compounds [140]. No work had been reported on the kinetics and mechanisms of CO substitutions of these compounds, so it was decided to mount such an investigation. Compounds, corresponding to known η^5-cyclopentadienyl metal carbonyls, were prepared and studied that have one heteroatom (N, P, or As) in the 5-membered ring.

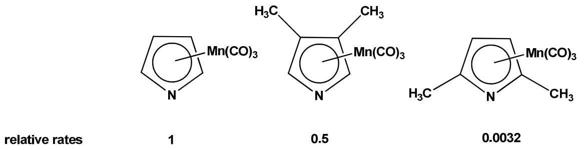
The reactions investigated [141] are presented in Scheme 28, where E = C, N, P or As, and L = PR$_3$ or P(OR)$_3$.



Scheme 28

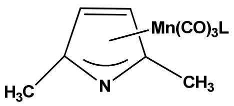
The compounds where E = C^{13}, P or As do not react even after 3 days at 130 ^{o}C. The (η^5-*N*-heterocycle)Mn(CO)$_3$ does reaction at these conditions with a second order rate law, first order in concentrations of the complex and of the nucleophile. Values of second order rate constant at 130^{o}C in decalin are 1.2 x 10^{-6} Mol^{-1}Lit Sec^{-1} for the nucleophile P(n-Bu)$_3$ and 2.0 x 10^{-6} mol^{-1}.L. sec^{-1} for P(OEt)$_3$. The tentative interpretation given these observations that only the *N*-heterocyclic compound reacts is that N is the most electronegative atoms used, e. g. N, 3.0; C, 2.5; P, 2.1; As, 2.0. Again the greater electron withdrawing property of the cyclic ligand with the more electronegative N atoms seems to enhance the rate of an η^5→ η^3→ η^5 mechanism.

Another interesting observation [142] was made when the rates of reaction of three (η^5-*N*-heterocyclic)Mn(CO)$_3$ were compared (Scheme 29).



Scheme 29

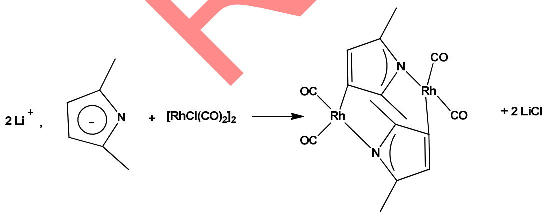
Addition of two methyl substituent which are electron donating to the pyrrolyl ligand are expected to decrease the rate of CO substitution by an associative $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$mechanism. What was not anticipated is that the positions of the methyl groups on the ring would have such a large effect, the 2,5-dimethyl pyrrolyl decreases the rate of substitution 100 times more than does the 3,4-dimethyl pyrrolyl. We suggest this results form a preferred ring slippage towards the formation of an η^3-2-azaallyl bonding mode of the metal moiety to the pyrrolyl ligand (Scheme 30) in the transition state or active intermediate for reaction.



Scheme 30

This slippage towards nitrogen results in a much more crowded transition state for (I) than for the corresponding 3,4-dimethylpyrrolyl system, and thus a much greater retardation in the rate of CO substitution, Support for ring slippage towards N is provided [143] by the X-ray structure of (η^5-3,4-dimethylpyrrolyl)Mn(CO)$_3$which shows such slippage even in the ground state.

Since only the *N*-heterocycle compounds (η^5-*N*-heterocycle)Mn(CO)$_3$react rapidly enough even at 130^{o}C to conduct a kinetic study, it has not been possible to determine if indeed there is a quantitative correlation between the rates of CO substitution and the electronegativity of the hetero atom. This should be possible providing we could prepare the more reactive compounds of the type (η^5-heterocycle)M(CO)$_2$, where M = Co, Rh, or Ir. An attempt (Scheme 31) [144] was made to prepare (η^5-2,5-dimethylpyrrolyl)Rh(CO)$_2$by a reaction analogous to that used for the synthesis of (η^5-C$_5$H$_5$)Rh(CO)$_2$.



Scheme 31

The desired and expected monomeric (η^5-2,5-(CH$_3$)$_2$C$_4$H$_2$N)Rh(CO)$_2$was not obtained, so we have as yet been unable to test the concept of reactivity versus the electronegativity of the heteroatom. However, the dimer obtained is the first example of a heterocyclic bridging ligand between two metals utilizing both the σ and the η^2-π bonding modes of the ligand to form a highly distorted metal-olefin moiety.

3.3. 17-electron metal complexesmechanism

It is well known that for molecular transition metal organometallic compounds 18-electrons is the magic number for maximum stability. Three decade ago Brown [145] reported that 17-electron metal carbonyl radicals, such as Mn(CO)$_5$ and Re(C0)$_5$, are substitution labile. These radicals were generated photochemically in solution and studied in situ, so Shi & Richmond [146] decided to investigate V(CO)$_6$ which is a stable solid 17-electron binary metal carbonyl (Scheme 32).

$$V(CO)_6 + L \longrightarrow V(CO)_5L + CO$$

Scheme 32

The reaction proceeds by an associative mechanism. The point of interest here is that it was possible for the first time to quantitatively compare the rates of CO substitution of analogous 17- and 18-electron metal carbonyls (Scheme 33).

	Cr(CO)$_6$	V(CO)$_6$
	18-electrons	17-electrons
relative rates	1	10^{10}

Scheme 33

This rapid rate of associative ligand substitution of a 17-electron over a corresponding 18-electron metal complex is in accord with the lower energy barrier for the reaction process of 17-electron →19-electron compared to that of 18-electron →20-electron.

This investigation was extended to the reaction of vanadocene, (η^5-C$_5$H$_5$)V, with CO to give the 17-electron adduct (η^5-C$_5$H$_5$)$_2$VC0 and to its CO exchange kinetics [147]. The rate of CO exchange is fast and it goes by an associative mechanism as proposed by the reaction profile.

Experiments showed that the rate of CO exchange with (η^5-C$_5$H$_5$)VCO is greater than the rate of addition of CO to vanadocene, which accounts for the higher energy barrier. It is believed this is caused by the conformational change required when CO is added to vanadocene, whereas the associative CO exchange takes place without the expenditure of energy required to bend back the cyclopentadienyl rings.

A dramatic change in rate and in mechanism was observed [148] when cyclopentadienyl was replaced by pentadienyl in these systems. The compound (η^5-C$_5$H$_7$)VCO is substituted inert and substitution takes place by a dissociative pathway.

This is the first report of a kinetic study of a 17-electron organometallic compound that is slow to react and that reacts by a dissociative process. The absence of a facile associative substitution pathway in the pentadienyl compounds may be attributed to the more rigid (η^5-C$_5$H$_7$)$_2$V moiety, decreased V-CO π-backbonding, or reduced electron spin delocalization, all of which make the meral center less susceptible to nucleophilic attack.

4. Previously reported substituted complexes of G-6 metal carbonyls

4.1. Metal carbonyl complexes with monodentate ligands

The photochemical reactions of W(CO)$_6$ with alkynes HC≡CH, HC≡CMe and HC≡CCMe$_3$ give the unstable terminal alkyne complexes [W(CO)$_5$(η^2-HC≡CR)], [W(CO)$_4$(η^2-HC≡CR)$_2$], [W(CO)(η^2-HC≡CR)$_3$], and vinylidene derivatives [W(CO)$_5$(C=CHR)].

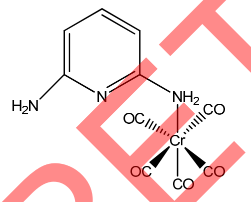
The studies show that alkynes behave as monodentate ligand [149]. The metal carbonyl complexes with various monodentate ligands are shown below.

4.1.1. Monosubstituted complexes [M(CO)$_5$L]

A series of carbonylchromium, molybdenum and tungsten complexes containing ferrocenylpyrazole ligands, (M(CO)$_5$L) (M=Cr, Mo or W; L represents ferrocenyl pyrazole), have been prepared by the photochemical reactions of ferrocenylpyrazole ligands with M(CO)$_6$ [150]. Tetraazaadamantane (taad) reacts with Group-VI metal hexacarbonyls to give homonuclear (taad)M(CO)$_5$ (M= Cr, Mo and W) derivatives [151]. [M(CO)$_4$**L**] (M = Cr, Mo or W; **L** = 1,5-Diselena-5-ferrocenophane) have been prepared. The structures of [M(CO)$_4$**L**] (M = Cr, Mo) show that **L** adopts the unusual *meso*-2 conformation [152].

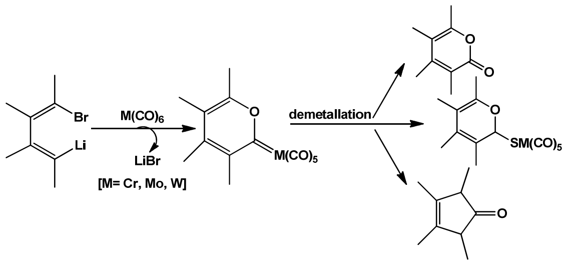
Thermal reactions of the metal hexacarbonyls M(CO)$_6$ (M = Cr, Mo but not W) with tris(dimethylamino)arsine (Tdas) give monosubstituted derivatives TdasM(CO)$_5$ (M = Cr, Mo) [153]. [M(CO)$_5$(DTTT)] [M=Cr; Mo; W], have been synthesized by the photochemical reaction of metal carbonyls [M(CO)$_6$] (M=Cr, Mo and W), with 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (DTTT). The spectroscopic studies show that DTTT behaves as a monodentate ligand coordinating via the sulfur (C=S) donor atom [154]. M(CO)$_5$(2-aminoazole), where M = Cr or W, showed preferred endocyclic imine coordination when provided with endocyclic soft thioether or endocyclic hard amine, endocyclic borderline imine and exocyclic hard amine coordination sites [155].

The synthesis and spectroscopic data of six Group 6 metal complexes of type of M(P{R}{TMS}$_2$)(CO)$_5$, M = Cr, Mo, W; R = C$_6$H$_5$ and M = Cr; R = H with the silylphosphine ligands, P(C$_6$H$_5$){Si(CH$_3$)$_3$}$_2$ and P(H){Si(CH$_3$)$_3$}$_2$ are reported [156]. Photolysis of hexacarbonylchromium(0) in the presence of 2,6-diaminopyridine in toluene solution at 10 °C yields pentacarbonyl(2,6-diaminopyridine)chromium(0), which could be isolated from solution as plate-like crystals (Scheme 34). The 2,6-diaminopyridine ligand is bonded to the chromium atom through one of the NH$_2$ groups [157].



Scheme 34

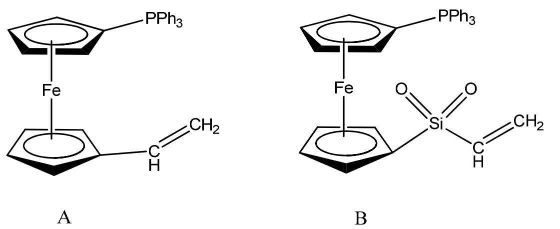
Fully alkyl substituted pyranylidene carbene complexes from M(CO)$_6$ (M = Cr, Mo, W) and the readily available 1-lithio-1,3-butadiene, bearing a leaving group, via an intramolecular trapping of metallaacylate intermediates. These carbenes have been demonstrated to have interesting and unique reactivity (Scheme 35) [158].



Scheme 35

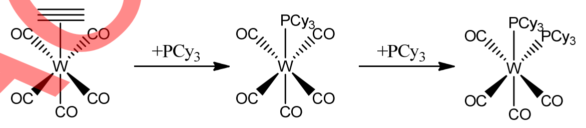
4.1.2. Bisubstituted complexes [M(CO)$_4$L$_2$]

Tungsten(0) carbonyl complexes with 1-(diphenylphosphanyl)-1′-vinylferrocene (Scheme 36 (A)) and 1-(diphenylphosphanyl)-1′-(dimethylvinylsilyl)ferrocene (Scheme 36 (B)) as P-monodentate donors, [W(CO)$_4$(L-κ*P*)$_2$], have been prepared [159].



Scheme 36

A series of germylene and stannylene (Me$_2$NCH$_2$CH$_2$O)$_2$E (E = Ge, E = Sn) complexes of group 6 metals carbonyls L·M(CO)$_n$ (M = Cr, Mo, W, n = 5 or 4)were prepared [160]. The pentacarbonyl(η^2-*bis*(trimethylsilyl)ethyne)tungsten(0), W(CO)$_5$(η^2-btmse), reacts with tricyclohexylphosphine, PCy$_3$, to yield W(CO)$_5$(PCy$_3$) and W(CO)$_4$(PCy$_3$)$_2$. The former complex is the alkyne substitution product, while the latter one is formed from the conversion of its labile *cis*-isomer, which is generated by further reaction of the CO substitution product, *cis*-W(CO)$_4$(η^2-btmse)(PCy$_3$), with a second PCy$_3$ molecule (Scheme 37) [161].



Scheme 37

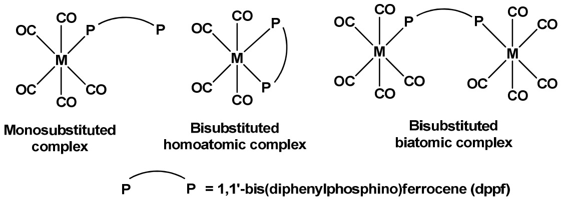
In *trans*- [Mo(CO)$_4$(PPh$_3$)$_2$], little deviation from ideal octahedral geometry is seen and the Mo---P bond length of 2. 500(1) Å is significantly shorter than those found in the *cis* isomer [162]. Reaction of norbornadiene complex C$_7$H$_8$Cr(CO)$_4$ with tris(dimethylamino)arsine (Tdas) at room temperature gives trans-(Tdas)$_2$Cr(CO)$_4$ which was isolated as yellow complex. Reactions of disubstituted derivatives trans-(Tdas)$_2$Cr(CO)$_4$ with carbonmonoxide at room temperature and pressure gives monosubstituted derivatives (Tdas)Cr(CO)$_5$ [63].

4.1.3. Trisubstituted complexes [M(CO)$_3$L$_3$]

The trisubstituted metalcarbonyl complexes containing ligands which coordinate through bicovalent sulfur are reported. Direct reaction of the ligands with cycloheptatrienemolybdenumtricarbonyl, Mo(CO)$_3$L$_3$ were prepared where L representing dimethyl sulfide [(CH$_3$)$_2$S], diethyl sulfide [(C$_2$H$_5$)$_2$S], thiourea [(CH$_2$)$_2$CS], thioacetamide [CH$_2$CSNH$_2$]. The thiourea and thioacetamide compounds are stable for periods of atleast a year in vacuum and for a week or move in the air under normal laboratory condictions. The diethylcomplexes are stable for at least a few weeks in vacuum but decompose within a few hours in air. The dimethyl sulfide compounds is immediately decomposed by air and is stable for few hours under vacuum [126].

4.2. Metal carbonyl complexes with bidentate ligands

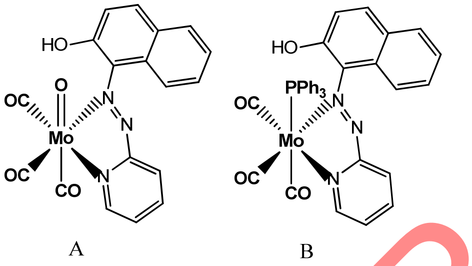
The metal carbonyl complexes with bidentate ligands are variety of homo- and bimetallic metal carbonyl compounds (Scheme38). Amanda*et al.* investigated metal carbonyl complexes containing 1,1‘-*bis*(diphenylphosphino)ferrocene (dppf) with the general formulas $M(CO)_5(dppf)$ (1a–c), $M(CO)_4(dppf)$ (2a–c), and $(CO)_5M(dppf)M'(CO)_5$ (3a–f) (M, M‘ = Cr, Mo, W) [163].



Scheme 38

4.2.1. Mononuclear complexes [M(CO)$_4$L]

Interaction of 1-(2-pyridylazo)-2-naphthol (PAN) with $[Mo(CO)_6]$ in air resulted in formation of the tricarbonyl oxo-complex $[Mo(O)(CO)_3(PAN)]$ (Scheme 39(A)). In presence of triphenyl phosphine (PPh_3), the reaction of PAN with either $Mo(CO)_6$ or $Ru_3(CO)_{12}$ gave $[Mo(CO)_3(PAN)(PPh_3)]$ (Scheme 39(B)), and $[Ru(CO)_2(PAN)(PPh_3)]$. Taher *et al.* reported that PAN behaves as a bidentate ligand coordinating via the two N donor atom [164].

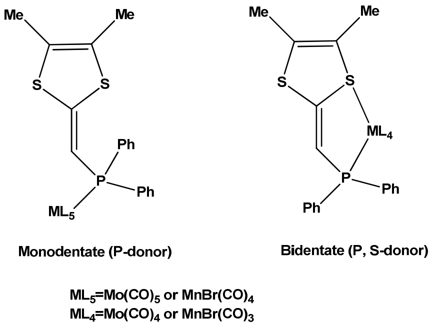


Scheme 39

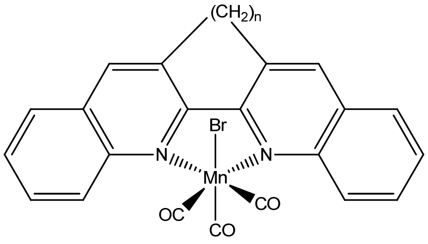
The ability of the dithiafulvenylphosphine (P-DTF) to react as a monodentate (P) or a bidentate (P,S) ligand with metal carbonylcomplexes such as $Mo(CO)_6$ and $MnBr(CO)_5$ was investigated (Scheme 40) [165].

The reaction of *bis*(3,5-dimethyl-1,2,4-triazol-1-yl)methane, $CH_2(3,5\text{-}Me_2Tz)_2$, with $M(CO)_6$ (M=Cr, Mo or W) in refluxing DME produces $CH_2(3,5\text{-}Me_2Tz)_2M(CO)_4$ in moderate yield [166].

Metal carbonyl complexes $MnBr(CO)_3$(3,3′-R-2,2′-biquinoline) containing heterocyclic nitrogen ligands (3,3′-R-2,2′-biquinoline) (R=CH_3 and CH_3; H and H; ---CH_2---CH_2--- or ---CH_2---CH_2---CH_2---) were synthesized. The ligand (3,3′-R-2,2′-biquinoline) behave as bidentate ligand coordinating via two N donor atoms (Scheme 41) [167].

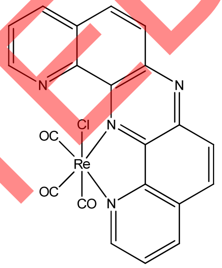


Scheme 40



Scheme 41

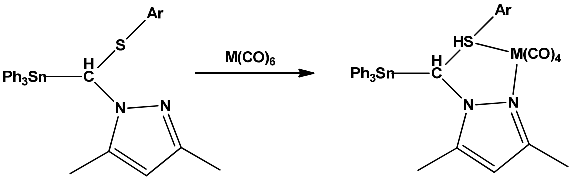
The synthesis of metal carbonyl complexes containing the heterocyclic nitrogen ligand 4′-phenyl-2,2′:6′,2″-terpyridine are reported. Complexes of the $[M(CO)_4(L)]$ type (M= Mo(0), or W(0); and L=4′-phenyl-2,2′:6′,2″-terpyridine) were prepared by photosubstitution or by thermolytic reactions [168]. Re(I) carbonyl complex *fac*- $[Re(CO)_3(dpop')Cl]$ with the nominally bi-dentate ligand dipyrido(2,3-*a*:3′,2′-*j*)phenazine (dpop′) were prepared (Scheme42) [169].



Scheme 42

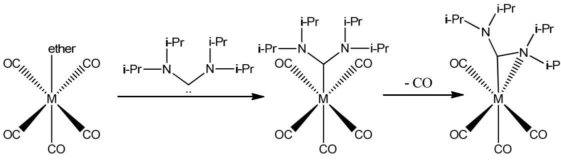
Tungsten(0)-carbonyl complexes of naphthylazoimidazoles $[W(CO)_5$(α-NaiR-N)] are reported. The complexes have been transformed to $[W(CO)_4$(α-NaiR-N,N′)] at higher temperatures where α-NaiR-N dentes a monodentate imidazole-N donor ligand and α-NaiR-N,N′ denotes a bidentate imidazole-N, azo-N donor ligand [170]. The chiral diimine ligand $C_5H_4N\text{-}2\text{-}C(C_6H_5)\text{=}N\{(1S,2S)\text{-}C_5H_8\text{-}2\text{-}OCH_2C_6H_5)\}$ was prepared via the reaction of 2-benzoyl pyridine and (1*S*,2*S*)-(+)-2-benzyloxycyclopentylamine. The ligand reacts with $M(CO)_6$ in toluene to give the respective chiral metal(0) complexes $[M(CO)_4$(L-κ*N*,*N*′)] (M = Mo and W) [171].

N,*N*′-Bis(ferrocenylmethylene)ethylenediamine (bfeda) yields $M(CO)_4$(bfeda) complexes (M = Cr, Mo, W) which could be isolated. In the case of tungsten, $W(CO)_5$(bfeda) is formed as intermediate and then undergoes the ring closure reaction yielding the ultimate product $W(CO)_4$(bfeda) [172]. Upon treatment of functionalized ligands $Ph_3SnCH(SPh)(3,5\text{-}Me_2Pz)$ and $Ph_3SnCH(SPy)(3,5\text{-}Me_2Pz)$ (Pz = pyrazol-1-yl and Py = 2-pyridyl) with group 6 metal carbonyl complexes, markedly different reactions are observed. Reaction of 1-arylthiomethyl-3,5-dimethylpyrazole $[ArSCH_2(3,5\text{-}Me_2Pz)$, Ar = phenyl or 2-pyridyl, Pz = pyrazol-1-yl] with $Mo(CO)_6$ produces complexes $ArSCH_2(3,5\text{-}Me_2Pz)Mo(CO)_4$, while similar reaction with $W(CO)_6$ yields analogous complexes $ArSCH_2(3,5\text{-}Me_2Pz)W(CO)_4$ (Scheme 43) [173].



Scheme 43

The $Mo(CO)_4DAB$ where DAB= diacetyldihydrazone, glyoxalcyclohexylamine, diazabutadiene were prepared where DAB behave as bidentate ligand [174]. Reaction of *bis*(diisopropylamino)carbene with ether substituted Mo-, and W-carbonyls leads to η^2-bonded carbene complexes which can be converted in contrast to the analogous chromium complex in a CO-atmosphere to imine complexes (Scheme 44) [175].



Scheme 44

The complexes $[M(CO)_4(\eta^2\text{-}H_2L)]$ [M = Cr; Mo; W] have been synthesized by photochemical reactions of VIB metal carbonyls $[M(CO)_6]$ [M = Cr; Mo; W] with *N,N'*-*bis*(salicylidene)-1,2-*bis*-(*o*-aminophenoxy)ethane (H_2L) in THF. The H_2L ligand was found coordinated to the central metal as bidentate ligand via the central azomethine nitrogen atoms [176]. The interaction of the group VI metal hexacarbonyls with electron donors has been widely explored. These reaction generally require thermal activation, although in some cases photolytic activation was observed. Photolytic preparation of some new anionic derivatives of chromium, molybdenum and tungsten hexacarbonyls involving both the difluorodithiophosphate anion and difluorothiosulphate anion as ligands. The reaction between metal hexacarbonyl and complexing anion in methylene chloride solution results the formation of $M(CO)_4PF_2S_2^-$ complexes. These complexes were found to be air stable in solid state, although solutions are oxidized by atmospheric oxygen. The stability increases from chromium to tungsten derivatives [177].

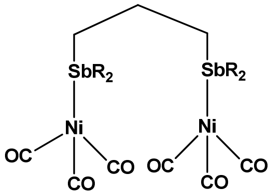
4.2.2. Binuclear complexes $[M_2(CO)_{10}L]$

Pentacarbonylpyrazinetungsten(0), $(CO)_5W(pyz)$, is not stable in solution in polar solvents such as acetone or dichloromethane and undergoes conversion to a bimetallic complex, $(CO)_5W(pyz)W(CO)_5$[178]. Density functional theory has been used to explore possible homoleptic binuclear Cr carbonyls $Cr_2(CO)_n$ (n = 11, 10, 9, and 8) using the pure DFT method BP86 and the hybrid Hartree-Fock DFT method B3LYP. The binuclear $Cr_2(CO)_{11}$ is computed to be thermodynamically unstable with respect to dissociation into mononuclear fragments. The following binuclear Cr carbonyls were found with metal-metal multiple bonding - $Cr_2(CO)_{10}$, $Cr_2(CO)_9$, and $Cr_2(CO)_8$ [179].

IR spectroelectrochemical studies of the metal carbonyl dimers $Mn_2(CO)_{10}$ and $[CpM(CO)_3]_2$ (M = W, Mo). Cross-coupling and ligand substitution reactions of electrochemically generated organometallic radicals were reported [180].

The transition metal carbonyl complexes of 1,3-bis(di-R-stibino)propanes (R = Me or Ph) (distibinopropanes) with the carbonyls of Cr, Mo, W, Fe, Mn and Ni were prepared. These include *cis*-$[M(CO)_4\{R_2Sb(CH_2)_3SbR_2\}]$ (M = Cr, Mo or W), $[\{Fe(CO)_4\}_2\{\mu\text{-}R_2Sb(CH_2)_3SbR_2\}]$, $[\{Ni(CO)_3\}_2\{\mu\text{-}R_2Sb(CH_2)_3SbR_2\}]$ (Scheme 45), $[Co_2(CO)_6\{Ph_2Sb(CH_2)_3SbPh_2\}]$, $[Co_2(CO)_4\{Me_2Sb(CH_2)_3SbMe_2\}_3]$ $[Co(CO)_4]_2$ and $[Mn_2(CO)_8\{Ph_2Sb(CH_2)_3SbPh_2\}]$. The studies show that distibinopropanes are bidentate ligands [181].

Sunlight irradiation of the reactions of $[M(CO)_6]$, M=Cr, Mo and W with dimethylglyoxime (H_2dmg) in THF were investigated. The reaction of $[Cr(CO)_6]$ with H_2dmg resulted in the formation of the square pyramidal complex $[CrO(H_2dmg)_2]$. The H_2dmg coordinated the metal from the two nitrogen atoms. The corresponding reactions of molybdenum and tungsten carbonyls yielded the binuclear oxo complex $[(H_2dmg)O_2M(\mu\text{-}O)_2MO_2(H_2dmg)]$ [182]. The structure, bonding, and photochemistry of the Group VI cyclopentadienyl metal carbonyl compounds of the general form $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$, where M=Cr, Mo, and W, and their ring-substituted and ring-coupled derivatives is critically reviewed [183].



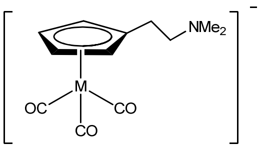
Scheme 45

Binuclear metal carbonyl complexes have been reported via cis-bridging bidentate coordination of the ligand between two metals in $\{M_2(CO)_4\ [\mu\text{-}Ph_2P(S)P(S)Ph_2]\}$(M = Cr, Mo and W) [184,185]. Lithiation of ligand CpPhCHCHPhCp and addition of $(MeCN)_3M(CO)_3$ (M = Mo, W) followed by oxidation with 2 equiv. of ferrocenium tetrafluoroborate, afford (PhCHCHPh)-coupled *bis*(cyclopentadienyl) dinuclear molybdenum and tungsten complexes [186].

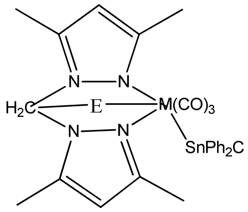
4.3. Metal carbonyl complexes with tridentate ligands

The bicyclic triene 5,6-dimethylenebicyclo [2.2.1]heptene-2 has been found to react with chromium, molybdenum and tungsten hexacarbonyls to produce volatile red-to-orange crystalline solids of composition $C_9H_{10}M(CO)_3$ [187]. Reactions of $M(CO)_6$, where M = Cr and Mo with Schiff bases prepared by the condensation of ethanolamine with either acetylacetone or benzoylacetone were investigated. The reactions of $Cr(CO)_6$ in benzene resulted in the formation of the tricarbonyl drivatives $[Cr(CO)_3(HL)]$, HL = acaceaH or baceaH. The HL proved to act as a tridentate ligand [188]. Salts of (2-(dimethylamino)ethyl)cyclopentadienyl (Cp^N) group VI metal carbonyl anions ($[M(CO)_3(\eta^5\text{-}Cp^N)]^-$ (M = Cr, Mo, W)) were reported (Scheme 46) [189].

The modification of *bis*(pyrazol-1-yl)methane by sulfur or selenium on the methine carbon has been successfully carried out by the reaction of the *bis*(pyrazol-1-yl)methide anion, prepared in situ by the reaction of bis(pyrazol-1-yl)methane with *n*-BuLi, with elemental sulfur or selenium. These bis(pyrazol-1-yl)methylthiolate(Scheme 47) or selenolate anions reacted with $M(CO)_6$ (M = Mo or W) in THF and formed their tricarbonyl metal anions$CH(Pz)_2EM(CO)_3^-$ [190].

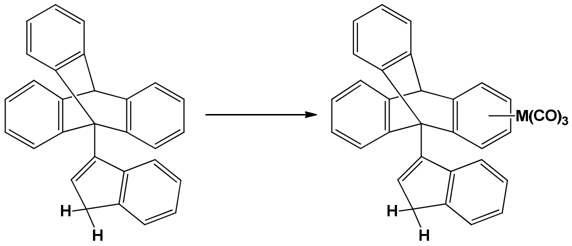


Scheme 46



Scheme 47

The potential use of haptotropic shifts to control rotational barriers has been initiated by the synthesis of (9-indenyl) triptycene and its chromium tricarbonyl derivative. In the metal complex, the chromium carbonyl moiety coordinates to one of the blades of the triptycene unit rather than to the more crowded indenyl group (Scheme48) [191].



Scheme 48

Organotransition-Metal Complexes of tridentate ligands were synthesized by Shiu and Chou and their structure and reactivity of first intramolecular coordination compound with weakely bound η^2-arene have been done. They found that thermolysis of $(PhHCPz'_2)Mo(CO)_4$ in DME gives $(PhHCPz'_2)Mo(CO)_3$ (Pz' = 3,5-dimethylpyrazol-1-yl) [192].

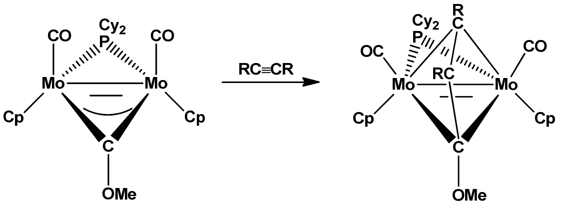
5. Some cluster complexes of G-6 metal carbonyl complexes

The phrase *cluster* was coined by F. A. Cotton in the early 1960s to refer to compounds containing metal-metal bonds. In 1990 Mingos and Wales explain cluster as a compound contains a group of two or more metal atoms where direct and substantial metal metal bonding is present [193]. A cluster is an ensemble of bound atoms intermediate in size between a molecule and a bulk solid. Transition metals and main group elements form strong clusters [194]. The main cluster types are "naked" clusters (without stabilizing ligands) and those with ligands. For transition metal clusters, typical stabilizing ligands include carbon monoxide, halides, isocyanides, alkenes, and hydrides. For main group elements, typical clusters are stabilized by hydride ligands. Transition metal clusters are frequently composed of refractory metal atoms. In general metal centers with extended d-orbitals form stable clusters because of favorable overlap of valence orbitals. Thus, metals with a low oxidation state for the later metals and mid-oxidation states for the early metals tend to form stable clusters. Polynuclear metal carbonyls are generally found in late transition metals with low formal oxidation states. Braunstein et al. gives a review of Metal clusters in chemistry [195].

Types of clusters formed by metal carbonyls: Generally the clusters referred to have more than one metal atom. These metal clusters may be homonuclear or heteronuclear.

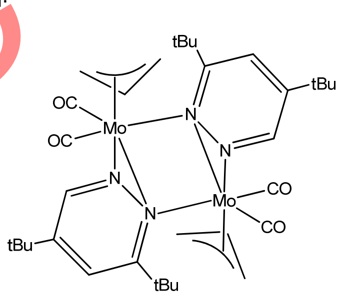
5.1. Homonuclear clusters

Homonuclear refers to a cluster with only one metal element. Dinuclear metal (I) carbonyl thiolates $[W_2(SPh)_2(CO)_8]$, $[Mo_2(SPh)_3(CO)_6]^-$, $[Mo_2(SPh)_2(CO)_6(S_2CNEt_2)]^-$, $[W_2(SPh)_2(CO)_6DPPM]$ and a polymer $[W_2(SPh)_2(CO)_6DPPM]_n$ were synthesized by the reaction of $M_2(SPh)_2(CO)_8]$ (M=Mo, W) with appropriate NaSR ($SR=SC_6H_5$, S_2CNEt_2) ligands in the presence of tetra-alkylammonium halide, or with diphenylphosphinemethane ($DPPM=(C_6H_5)_2P\ CH_2P\ (C_6H_5)_2$) in certain solvents [196]. The 32-electron complex $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(CO)_2]$ ($Cp = \eta^5\text{-}C_5H_5$) reacts at 333 K with terminal alkynes RC≡CR to give the corresponding derivatives $[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-}CRCHC(OMe)\}(\mu\text{-}PCy_2)(CO)_2]$, (R = *p*-tol, CO_2Me), with good yields (Scheme 49) [197].



Scheme 49

Di-nuclear molybdenum and tungsten metal cluster complexes $[Et_4N]_2[Mo_2(SC_6H_{11})_2(CO)_8]$, $[Et_4N][Mo_2(SC_6H_{11})_3(CO)_6]$, $[Ph_4P][Mo_2(SC_6H_{11})_3(CO)_6]$, $[(CH_3)_3PhCH_2N][Mo_2(SC_6H_{11})_3(CO)_6]$, $[Et_4N]_2[W_2(SC_6H_{11})_2(CO)_8]$, $[W_2(SC_6H_{11})_2(CO)_8]$ and $[Et_4N][W_2(SC_6H_{11})_3(CO)_6]$ had been synthesized with cyclohexanthiolate ligand [198]. Treatment of $M(allyl)(Cl)(CO)_2(py)_2$ (M = Mo, W) with 1 equiv. of potassium pyrazolates in tetrahydrofuran at −78 °C afforded $M(allyl)(R_2pz)(CO)_2(py)_n$ (R_2pz = 3,5-disubstituted pyrazolate; *n* = 1, 2; R= t-Bu) in 68-81% yields. Analogous treatment of $Mo(allyl)(Cl)(CO)_2(NCCH_3)_2$ with 1 equiv. of potassium pyrazolates (R_2pz where R= t-Bu) in tetrahydrofuran at −78 °C afforded $[Mo(allyl)(R_2pz)(CO)_2]_2$ in 79% yield (Scheme 50). An X-ray crystal structure analysis of $[Mo(allyl)(R_2pz)(CO)_2]_2$ showed a dimeric structure bridged by two $\mu\text{-}\eta^2\text{:}\eta^1\text{-}tBu_2pz$ ligands [199].



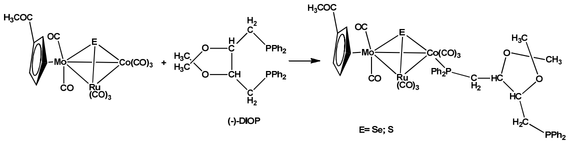
Scheme 50

Formation of carbonylrhenium cryptates with alkali metal cations was studied. Coordination chemistry studies of $[Ph_2P(E)NP(E)Ph_2]^-$, E = O, S, Se towards $ReBr(CO)_5$ were key target of the study in last decade. The reaction of $ReBr(CO)_5$ with $Li[Ph_2P(O)NP(O)Ph_2]$ afforded the cryptate $Li[Re_2(CO)_6\{\mu\text{-}Ph_2P(O)NP(O)Ph_2\text{-}\kappa^2 O,O'\}_3]$; whereas $K[Ph_2P(O)NP(O)Ph_2]$ reacted with $ReBr(CO)_5$ to give $K[Re_2(CO)_6\{\mu\text{-}Ph_2P(O)NP(O)Ph_2\text{-}\kappa^2 O,O'\}\{Ph_2P(O)NP(O)Ph_2\text{-}\kappa^2 O,O'\}_2]$. Other chalcogen ligands' salts M $[Ph_2P(E)NP(E)Ph_2]$, E = Se and S, M = K and Li gave dirhenium carbonyls with bromido and $Ph_2P(E)NP(E)Ph_2$, E = Se or S bridges upon reaction with $ReBr(CO)_5$ [200].

5.2. Heteronuclear clusters

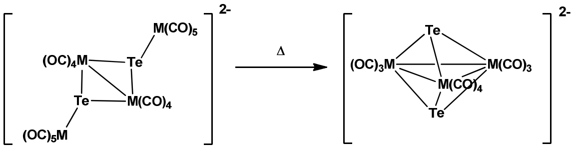
Heteronuclear refers to a cluster with at least two different metal elements. These complexes are also known as mixed metal complexes. The oxygen transfer reaction of the heterometallic carbonyl cluster $(\mu_3\text{-}S)FeCo_2(CO)_9$ with *bis*(*p*-methoxyphenyl)telluroxide (BMPTO) gives *bis*(*p*-methoxyphenyl)telluride (BMPT) coordinated metal cluster products $(\mu_3\text{-}S)FeCo_2(CO)_8(BMPT)$ and $(\mu_3\text{-}S)FeCo_2(CO)_7(BMPT)_2$, which react further with PPh_3 to afford Ph_3P-substituted derivatives $(\mu_3\text{-}S)FeCo_2(CO)_8(PPh_3)$ and $(\mu_3\text{-}S)FeCo_2(CO)_7(PPh_3)_2$, respectively [201]. Mixed-metal tetrahedral clusters $[(\mu_3\text{-}E)RuCoMo(CO)_7(CpC(O)CH_3)][(\text{-})\text{-}DIOP]$ (E=Se, S) were obtained by the reactions of $[(\mu_3\text{-}$

E)$RuCo_2(CO)_9$] (E=Se, S) and [(μ_3-E)$RuCoMo(CO)_8(CpC(O)CH_3)$] (E=Se, S) with the diphosphine compound (-)-DIOP [(2,2-dimethyl-1,3-dioxolane-4,5-diyl *bis*-methylene)bisdiphenyl-phosphine] in *n*-hexane or THF at room temperature, respectively (Scheme 51) [202].



Scheme 51

The tellurium-containing trigonal bipyramidal clusters $[Te_2CrM_2(CO)_{10}]^{2-}$ (M = Cr; Mo; W) has been synthesized from the ring closure reactions of the ring complexes $[Te_2Cr_2M_2(CO)_{18}]^{2-}$ (M = Cr; Mo; W) (Scheme 52) [203].



Scheme 52

Selenium-capped trimolybdenum and tritungsten ring carbonyl clusters $[Se_2M_3(CO)_{10}]^{2-}$ (M = Mo, W)have been synthesized (Figure 8). These selenium-capped trimolybdenum cluster compound $[Et_4N]_2$ $[Se_2Mo_3(CO)_{10}]$ ($[Et_4N]_2$) can be obtained from the reaction of the trichromium cluster compound $[Et_4N]_2$ $[Se_2Cr_3(CO)_{10}]$ with 4 equiv. of $Mo(CO)_6$ in refluxing acetone. On the other hand, when $[Et_4N]_2$ $[Se_2Cr_3(CO)_{10}]$ reacted with 4 equiv. of $W(CO)_6$ in refluxing acetone, the planar cluster compound $[Et_4N]_2$ $[Se_2W_4(CO)_{18}]$ ($[Et_4N]_2$) was isolated, which could further transform to the tritungsten cluster compound $[Et_4N]_2$ $[Se_2W_3(CO)_{10}]$ ($[Et_4N]_2$) in good yield. Alternatively, these clusterscould be formed from the reactions of the monosubstituted products $[Et_4N]_2$ $[Se_2Cr_2M(CO)_{10}]$ (M = Mo; W, $[Et_4N]_2$) with 3 equiv. of $M(CO)_6$ in acetone, respectively [204].

2,2′-Bipyrimidine metal multinuclear complexes [($(CO)_4Mo$)(μ-1,2,3,4-bipym)$Pt(C\equiv CFc)_2$] with $Mo(CO)_6$ have been synthesized originating from *cis*- [(bipym)$Pt(C\equiv CR)_2$] (R = $SiMe_3$) in presence of tetrahydrofuran after irradiation for 16 h at 25 °C [186]. Thermolysis of a toluene solution containing [$Fe_2W(CO)_{10}(\mu_3-S)_2$] (1) and [($\eta^5$-$C_5H_5$)$W(CO)_3(CCPh)$] (2), at 80°C yields the mixed metal cluster [$Fe_2(CO)_6(\mu_3-S)_2W\{(\eta^5-C_5H_5)W(CO)_3(CCPh)\}_2$] (Scheme 53) [205].

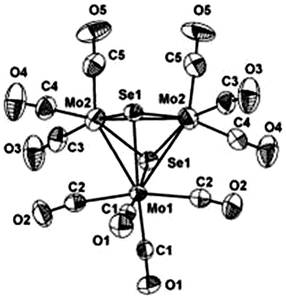
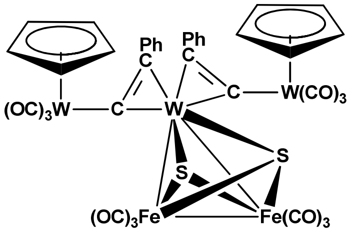
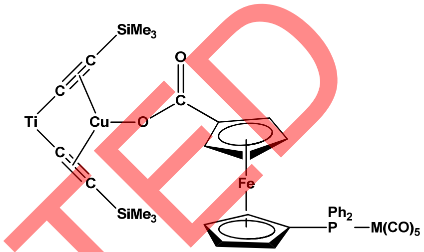


Figure 8. Selenium-capped trimolybdenum ring carbonyl clusters [204].



Scheme 53

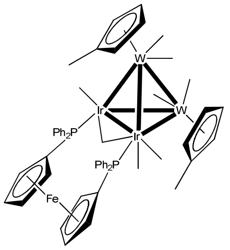
Reaction between $HO_2CfcPPh_2M(CO)_5$ (M = Cr, Mo, W; fc = ferrocene-1,1′-diyl) and { [Ti](μ-σ,π-$C\equiv CSiMe_3$)$_2$}CuMe at −30 °C gave the alkyne/ferrocene-bridged heterotetrametallic compounds {[Ti](μ-σ,π-$C\equiv CSiMe_3$)$_2$}$CuO_2CfcPPh_2M(CO)_5$ (M = Cr, Mo, W) (Scheme 54) [206].



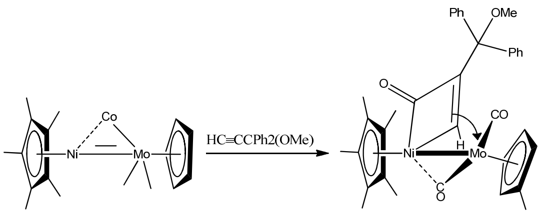
Scheme 54

The 60-electron tetrahedral clusters $W_2Ir_2(\mu-L)(CO)_8(\eta^5-C_5H_4Me)_2$ [L=dppe, dppf] (Scheme 55) have been prepared from reaction between $W_2Ir_2(CO)_{10}(\eta^5-C_5H_4Me)_2$ and the corresponding diphosphine in 52 and 66% yields, respectively [207].

Mixed ligand derivatives of $MoIr_3(\mu-CO)_3(CO)_8(\eta-C_5R_5)$ (R=H, Me) and $Mo_2Ir_2(\mu-CO)_3(CO)_7(\eta-C_5H_5)_2$ with stoichiometric amounts of the isocyanide Bu^tNC afford the ligand substituted cluster in fair to good yields (13-58%) [208]. Tetrahedral mixed-metal cluster $WIr_3(CO)_{11}(\eta-C_5H_4Me)$ is prepared in 8% yield from reactions between $[W(CO)_3(\eta-C_5H_4Me)]^-$ and $IrCl(CO)_2$(*p*-toluidine) under an Ar atmosphere, and in 46% yield from reaction between $WH(CO)_3(\eta-C_5H_4Me)$ and $IrCl(CO)_2$(*p*-toluidine) under a CO atmosphere. $WIr_3(CO)_{11}(\eta-C_5H_4Me)$ reacts with diphenylacetylene to afford three products, namely tetrahedral $WIr_3(\mu_3-\eta^2-PhC_2Ph)_2(CO)_7(\eta-C_5H_4Me)$, butterfly $WIr_3\{\mu-\eta^4-C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5(\eta-C_5H_4Me)$ and the binuclear product $Ir_2\{\mu-\eta^4-C(Ph)C(Ph)C(Ph)C(Ph)\}(CO)_5$ [209]. The nickel-molybdenum complex $[(\eta^5-C_5Me_5)Ni{=}Mo(CO)_3(\eta^5-C_5H_4Me)]$ can be considered to contain a partially dative nickel-molybdenum double bond. This complex reacts with the bulky terminal alkyne $HC\equiv CCPh_2(OMe)$ (DPMP) to afford the alkyne-carbonyl coupled metallacyclic product $[(\eta^5-C_5Me_5)Ni\{(\mu-CH{=}CR-C(O)\}Mo(CO)_2(\eta^5-C_5Me_5)]$ (Scheme 56) (R = $CPh_2(OMe)$, Ni-Mo) regioselectively and exclusively [210].

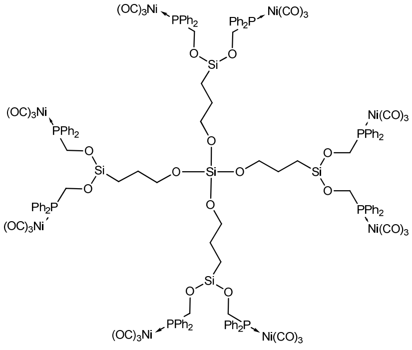


Scheme 55



Scheme 56

Branched dendritic metallo carbosiloxanes of type $Si(OCH_2CH_2CH_2SiMe_2[OCH_2PPh_2M(CO)_n])_4$ (n = 3: M = Ni; n = 4: M = Fe; n = 5: M = Mo, W) have also been prepared (Scheme 57). These molecules possess phosphorus-metal carbonyl groups as end-grafted units [211].



Scheme 57

5.3. Predicting structures of cluster compounds

The polyhedral skeletal electron pair theory or Wade's electron counting rules predict trends in the stability and structures of many metal clusters. The electron counting rules were originally formulated by Kenneth Wade and were further developed by D. M. P. Mingos and others; they are sometimes known as Wade's rules or the Wade/Mingos rules. The rules are based on a molecular orbital treatment of the bonding [212-215]. Recently these rules are extended and unified for macropolyhedral boranes, metallocenes and borides. The unified electron counting rules are called Jemmis *mno* rules [216-217].

Different rules (4n, 5n or 6n) are invoked depending on the number of electrons per vertex. The 4n rules are reasonably accurate in predicting the structures of clusters having about 4 electrons per vertex, as is the case for many boranes and carboranes. For such clusters, the structures are based ondeltahedra, which are polyhedrain which every face is triangular. The 4n clusters are classified as *closo-, nido-, arachno- or hypho-*, based on whether they represent a complete (*closo-*)deltahedron, or a deltahedron that is missing one (*nido-*), two (*arachno-*) or three (*hypho*) vertices.

However, hypho clusters are relatively uncommon due to the fact that the electron count is high enough to start to fill antibonding orbitals and destabilize the 4n structure. If the electron count is close to 5 electrons per vertex, the structure often changes to one governed by the 5n rules, which are based on 3-connected polyhedra. As the electron count increases further, the structures of clusters with 5n electron counts become unstable, so the 6n rules can be implemented. The 6n clusters have structures that are based on rings. A molecular orbital treatment can be used to rationalize the bonding of cluster compounds of the 4n, 5n, and 6n types.

5.3.1. 4n Rules

The following polyhedraare the basis for the 4n rules; each of these have triangular faces [218]. The number of vertices in the cluster determines what polyhedron the structure is based on. Prediction of polyhedron structure based on number of vertices in cluster id given in Table 7.

Table 7. Prediction of polyhedron structure based on number of vertices in cluster.

Number of vertices	Polyhedron
4	Tetrahedron
5	Trigonal bipyramid
6	Octahedron
7	Pentagonal bipyramid
8	D_{2d} (trigonal) dodecahedron
9	Tricapped trigonal prism
10	Bicapped square antiprism
11	Octadecahedron
12	Icosahedron (bicapped pentagonal antiprism)

Using the electron count, the predicted structure can be found. n is the number of vertices in the cluster. The 4n rules are enumerated in Table 8.

Table 8. Structure prediction using electron count.

Electron count	Name	Predicted structure
4n-2	Bicapped closo	n-2 vertex closo polyhedron with 2 capped faces
4n	Capped closo	n-1 vertex closo polyhedron with 1 face capped
4n+2	Closo	Closo polyhedron with n vertices
4n+4	Nido	n+1 vertex closo polyhedron with 1 missing vertex
4n+6	Arachno	n+2 vertex closo polyhedron with 2 missing vertices
4n+8	Hypho	n+3 vertex closo polyhderon with 3 missing vertices

When counting electrons for each cluster, the number of valence electrons is enumerated. For each transition metal present, 10 electrons are subtracted from the total electron count. For example, in $Rh_6(CO)_{16}$ the total number of electrons would be 6(9) + 16(2) - 6(10) = 86 - 6(10) = 26. Therefore, the cluster is a closo polyhedron because n = 6, with 4n + 2 = 26.
Other rules may be considered when predicting the structure of clusters:

1. For clusters consisting mostly of transition metals, any *main group elements* present are often best counted as ligands or interstitial atoms, rather than vertices.
2. Larger and more electropositive atoms tend to occupy vertices of high connectivity and smaller more electronegative atoms tend to occupy vertices of low connectivity.
3. In the special case of boron hydride clusters, each boron connected to 3 or more vertices has one terminal hydride, while a boron connected to 2 other vertices has 2 terminal hydrogens. If more hydrogens are present, they are placed in open face positions to even out the coordination number of the vertices.
4. For the special case of transition metal clusters, ligands are added to the metal centers to give the metals reasonable coordination numbers, and if any hydrogen atoms are present they are placed in bridging positions to even out the *coordination numbers* of the vertices.

In general, closo structures with n vertices are n-vertex polyhedra. To predict the structure of a nido cluster, the closo cluster with n + 1 vertices is used as a starting point; if the cluster is composed of small atoms a high connectivity vertex is removed, while if the cluster is composed of large atoms a low connectivity vertex is removed. To predict the structure of an arachno cluster, the closo polyhedron with n + 2 vertices is used as the starting point, and the n+1 vertex nido complex is generated by following the rule above; a second vertex adjacent to the first is removed if the cluster is composed of mostly small atoms, a second vertex not adjacent to the first is removed if the cluster is composed mostly of large atoms.

The bookkeeping for deltahedral clusters is sometimes carried out by counting skeletal electrons instead of the total number of electrons. The skeletal orbital (electron pair) and skeletal electron counts for the four types of deltahedral clusters are:

- n-vertex closo: (n+1) skeletal orbitals, (2n+2) skeletal electrons
- n-vertex nido: (n+2) skeletal orbitals, (2n+4) skeletal electrons
- n-vertex arachno: (n+3) skeletal orbitals, (2n+6) skeletal electrons
- n-vertex hypho: (n+4) skeletal orbitals, (2n+8) skeletal electrons

The skeletal electron counts are determined by summing the total of the following number of electrons:

- 2 from each BH unit
- 3 from each CH unit
- 1 from each additional hydrogen atom (over and above the ones on the BH and CH units)
- the anionic charge electrons

5.3.2. 5n Rules

As discussed previously, the 4n rule mainly deals with clusters with electron counts of 4n+k, in which approximately 4 electrons are on each vertex. As more electrons are added per vertex, the number of the electrons per vertex approaches 5. Rather than adopting structures based on deltahedra, the 5n-type clusters have structures based on a different series of polyhedra known as the 3-connectedpolyhedra, in which each vertex is connected to 3 other vertices. The common types of 3-connected polyhedra are listed in Table 9.

Table 9. Prediction of polyhedron structure based on number of vertices in cluster.

Number of vertices	Type of 3-connected polyhedron
4	Tetrahedron
6	Trigonal prism
8	Cube
10	Pentagonal prism
12	D_{2d} Pseudo-octahedron

Using the electron count, the predicted structure can be found. n is the number of vertices in the cluster. The 5n rules are given in Table 10.

Table 10. Structure prediction using electron count.

Total electron count	Predicted structure
5n	n-vertex 3-connected polyhedron
5n+1	n-1 vertex 3-connected polyhedron with one vertex inserted into an edge
5n+2	n-2 vertex 3-connected polyhedron with two vertexes inserted into edges
5n+k	n-k vertex 3-connected polyhedron with k vertexes inserted into edges

5.3.3. 6n Rules

As more electrons are added to a 5n cluster, the number of electrons per vertex approaches 6. Instead of adopting structures based on 4n or 5n rules, the clusters tend to have structures goverened by the 6n rules, which are based on rings. The rules for the 6n structures are given in Table 11.

Table 11. Structure prediction using electron count.

Total electron count	Predicted structure
6n-k	n-membered ring with k/2 trans-annular bonds
6n-4	n-membered ring with 2 trans-annular bonds
6n-2	n-membered ring with 1 trans-annular bond
6n	n-membered ring
6n+2	n-membered chain (n-membered ring with 1 broken bond)

6. Uses of G-6 metal carbonyl substituted complexes

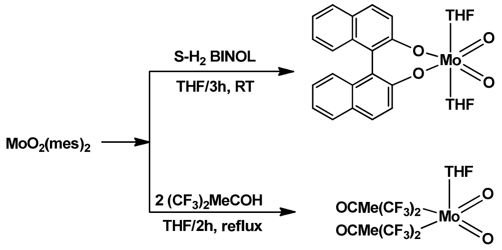
G-6 Metal hexacarbonyls are widely used in electron beam-induced deposition technique - these are easily vaporized and decomposed by the electron beam providing a convenient source of metal atoms [219].

6.1. As catalyst

$Mo(CO)_6$, $[Mo(CO)_3(MeCN)_3]$, and related derivatives are employed as catalysts in organic synthesis. For example, these catalysts can be used for alkyne metathesis and the Pauson-Khand reaction.

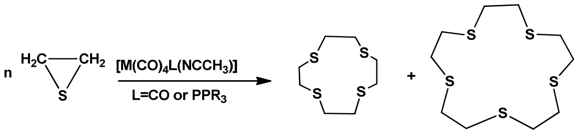
6.1.1. Metal carbonyl complexes as catalyst

Most of the existing metal carbonyl catalysts for acetylene polymerizations need to be preactivated by chlorine-containing additives or by UV irradiation in halogenated solvents. A series of "simple" metal carbonyl catalysts of general structure $M(CO)_xL_y$ (M = Mo, W; L= *bis*(trimethylsilyl)ethyne) were developed, none of which require additives or pre-photoirradiation, most of which are air- and moisture-stable, and some of which work well in nonhalogenated solvents [220]. Different catalyst derived from the reaction of Mo and dimethyl malonate such as $(CO)_{6-n}Mo(CHE_2)_n$ [221] or $(CO)_5Mo(CHE_2)$ [222-225]. Such catalysts appear to be of insufficient reactivity to initiate ionization. However, with the more reactive substrates, reaction proceeds normally [226]. Allylic alkylation catalyzed by molybdenum complexes like $Mo(bpy)(CO)_4$ [227,228], forms a useful and frequently complementary alternative to the palladium-catalyzed reactions. Higher selectivity for attack at primary vs. secondary carbon of a π-allyl fragment occurs with molybdenum catalyst. The synthesis of the dioxo-molybdenum(VI) and -tungsten(VI) derivatives MO_2(*S*-BINOL)$(THF)_n$ and MO_2 $[OCMe(CF_3)_2]_2(THF)$ (M = Mo, *n* = 2; W, *n* = 1) is reported (Scheme 58). André Pontes *et al.* have examined the potential of these complexes as catalysts for the sulfoxidation of methyl phenyl sulfide, olefin epoxidation and hydrosilylation of carbonyl groups [229].



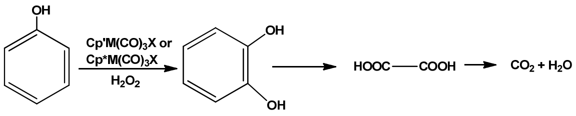
Scheme 58

Alkene carbonyl complexes of the type: $[M(CO)_5(\eta^2\text{-alkene})]$, $[M(CO)_4(\eta^2\text{-alkene})_2]$, and $[M(CO)_3(\eta^2\text{-alkene})_3]$ have been prepared by photochemical reactions of Group 6 transition metal carbonyls with alkenes. These complexes were found to exhibit some catalytic activity. These complexes catalyze to reactions that lead to the formation of new carbon-carbon bonds, such as metathesis, ring-opening metathesis polymerization of cyclic olefins (ROMP), and the addition of haloalkanes to the double bond of olefin [230]. The thiacrowns were synthesized by the catalytic ring opening cyclooligomerization of thiirane using some Group VI metal carbonyl complexes as catalyst. The Group VI catalyst precursors were transition metal complexes of the form $M(NCCH_3)(PR_3)_x(CO)_{5-x}$ (x=0, M=Cr, Mo and W; x=1, M=Cr, R=Ph; M=W, R=Ph, or OC_6H_4-p-Me). The yields of the thiacrowns were significantly improved by the addition of dialkyl acetylenedicarboxylates to the reactions catalyzed by the Group VI complexes (Scheme 59) [231].



Scheme 59

The catalytic activities of the complexes, $Cp'M(CO)_3X$ (Cp′ = Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5); M = Mo, W; X = Cl, CH_3) and $Mo(CO)_6$ have been examined for the oxidation of phenol (37. 6 g/L) using H_2O_2 as oxidant in aqueous solution (Scheme 60). Among them, $CpMo(CO)_3Cl$ and $CpMo(CO)_3(CH_3)$ showed the highest catalytic activity [232].



Scheme 60

6.1.2. Metal carbonyl cations as catalyst

Cationic metal carbonyls $[M(CO)_m]^{n+}$, which have a positive metal charge, were prepared from Cr, Ag, Au, Pd, Pt, Rh and Ir. The M-C bonds of these compounds were mainly formed by the σ-dative bond of CO, and then the ν co values were observed at a higher wavenumber than the free CO. These unstable cationic metal carbonyls were used as catalysts for the carbonylation of olefins, alcohols, dienes, aldehydes and saturated hydrocarbons to give *tert*-carboxylic acids in high yields at room temperature and atmospheric CO pressure [233].

There has been a rapid development in the study of metal carbonyl cations, which exhibit distinguishing characteristics in comparison with typical metal carbonyl complexes. Qiang Xu gives an overview of the catalytic application of metal carbonyl cations, including the metal carbonyl cluster cations [234].

6.1.3. Metal carbonyl clusters as catalyst

Catalytic activity of transition metalcarbonyl clusters substituted with benzyne (and, for comparison, benzene and diene) ligands was given by Sabrina Brait *et al.* Cluster-surface analogies are helpful in gaining an understanding of the homogeneous and heterogeneous catalytic behaviour of the clusters [235].

Molybdenum hexacarbonyl was immobilized on polystyrene (2% cross-linked with divinylbenzene) via imidazole linkage to obtain a polymer-supported molybdenum carbonyl catalyst (**2**). High conversion of a range of alkenes to epoxides was achieved with *tert*-butyl hydroperoxide and this catalyst. The catalyst is highly reusable and it was reused 10 times without a considerable change in its activity [236].

6.2. In nano science and nanotechnologies

The possible role of metal carbonyl clusters in nanoscience and nanotechnologies was investigated. Although a few nanosized metal carbonyl clusters (MCC) were already obtained in the seventies, these structurally and compositionally well-defined molecules attracted the interest of nanoscientists only as possible precursors of finely dispersed metal particles for heterogeneous catalysis. Cristina et al give a brief account of most recent results in the field of high-nuclearity metal carbonyl clusters and their emerging properties. In doing that, a look to related behaviour of ligand-stabilised and ligand-free clusters (Figure 9), including almost mono-dispersed ligand-stabilised metal nanoparticles, should be done. They found contribution of metal carbonyl clusters to some aspects of nanoscience and nanotechnologies also [237].

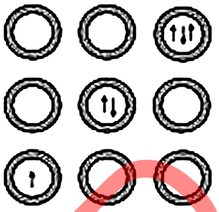


Figure 9. An ordered monolayer of differently charged individual MCC capacitors in consequence of their electron-sink properties and the insulating behavior of their CO shell [237].

An approach to noble metal-metal oxide dumbbell nanoparticles based on seed-mediated growth (Figure 10). Metal oxides are grown over the presynthesized noble metal seeds by thermal decomposition of metal carbonyl followed by oxidation in air. The as-synthesized dumbbell nanoparticles have intrinsic epitaxial linkage between the metal and the oxide, providing enhanced heterojunction interactions [238].

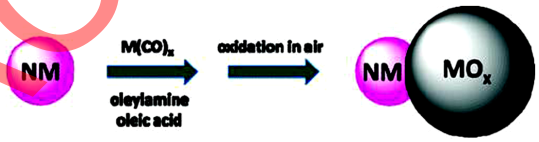


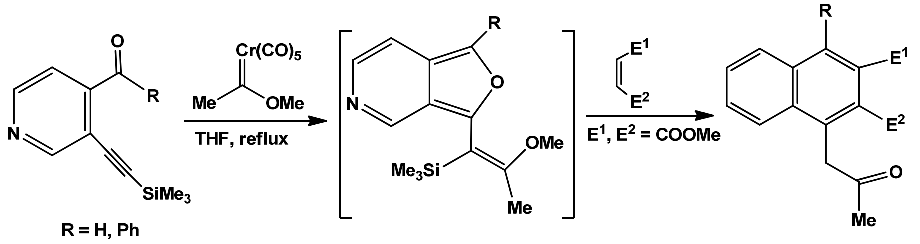
Figure 10. Metal carbonyl catalyzed reaction: Preparation of metal-metal oxide dumbbell nanoparticles [238].

6.3. In pharmaceuticals

Metal carbonyls and their use as a new class of pharmaceuticals were studied [239]. The hydrogenase enzymes contain CO bound to iron, apparently the CO stabilizes low oxidation states which facilitates the binding of hydrogen [240,241]. Certain metal carbonyls have been observed in trace amounts in landfills, where the reducing environment is compatible with their formation [242]. Metal carbonyls have extensively shown various antimicrobial activity against *E. coli, S. aureus, B. subtilis, P. vulgaris* etc. bacteria, *C. albicans, T. rubrum, T. mentagrophytes, A. niger*etc. fungi, *Cucumber mosaic* virus, insecticidal activity and plant growth inhibitory activity on rice, wheat and barley plants. Metal carbonyl complexes also shown antitherapeutic activities like antitumor and cytotoxic activities [242].

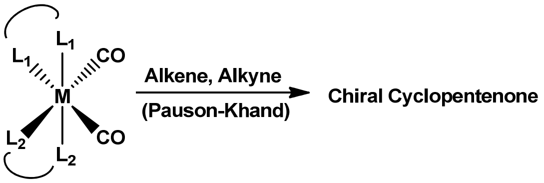
6.4. In synthesis of other complexes

Metal carbonyls are found their important role in finding some specific products. Photochemical reactions of ferrocenylacetylene with sulfur in presence of $Mo(CO)_6$ gives 2,5-diferrocenylthiophene and, with $Cr(CO)_6$, 2,6-diferrocenyldithiine formed. Formation of ferrocenyl-substituted thioketone complexes was observed in the reaction of ferrocenylacetylene with water and sulfur, in presence of $W(CO)_6$ [243]. Darensbourg reported the group 6 pentacarbonyl hydrides and various methods for their synthesis [244-246].



Scheme 64

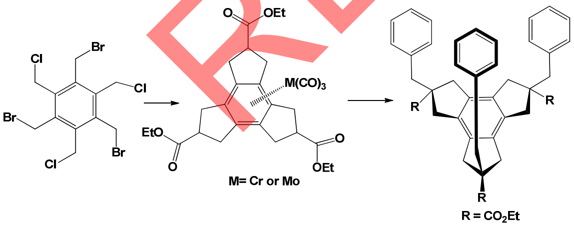
A major challenge that must be met for an asymmetric intermolecular Pauson-Khand reaction is to be able to limit the possible positions on the metal complex for the organic partners. Toward this end, the synthesis of monometallic systems derived from $M(CO)_6$ and two bidentate ligands, in which the number of possible coordination sites is reduced to two this lead to enantioselective Pauson-Khand reactions resulting the formation of Chiral Cyclopentanones (Scheme 61) [247].



Scheme 61

New polynuclear lanthanide(III) ionic clusters of general formula $[Ln_9(acac)_{16}(OH)_{10}]^+$ $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ (Ln = Sm, Eu, Gd, Dy, Yb) and $[Sm_9(acac)_{16}(OH)_{10}]^+$ $[CrW(CO)_{10}(\mu\text{-}H)]^-$ is reported. The polynuclear complexes, prepared under pure nitrogen atmosphere by interaction of the hydridic metal carbonyls with the β-dichetonate $Ln(acac)_3{\cdot}3H_2O$ (Ln = Sm, Eu, Gd, Dy, Yb) [248].

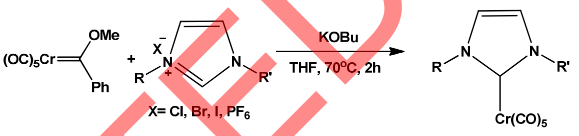
Novel C_{3V}-symmetric scaffold, trindane has been efficiently synthesized from 1,3,5-*tris*(bromomethyl)-2,4,6-tris(chloromethyl)benzene in six steps with 47% overall yield. The control of all-*syn*stereochemistry in the tribenzylation step has been achieved by blocking one side of the trindane ring by metal carbonyl complexes (Scheme 62) [249].



Scheme 62

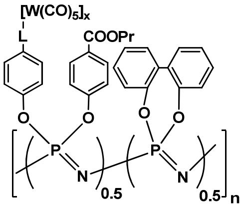
Chromium Fischer carbene complexes, $[Cr\{=OMe(R)\}(CO)_5]$ have been utilized as a source of chromium carbonyls in the synthesis of chromium NHC (*N*-heterocyclic carbene) complexes (Scheme 63). The method can be employed for the synthesis of molybdenum and tungsten NHC compounds [250].

The reaction of Fischer carbene complex with *o*-alkynylpyridine carbonyl derivatives involves the generation of furo [3,4-*c*]pyridine as transient intermediates through the coupling of *o*-alkynylpyridine carbonyl derivatives with carbene complex and subsequent Diels-Alder trapping with suitable dienophiles resulted in the formation of isoquinoline derivatives and the entire sequence can be run in one pot (Scheme 64). When an olefinic tether was present, intramolecular Diels-Alder cycloaddition occurred followed by ring opening to yield tricyclic alcohols [251].



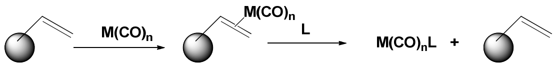
Scheme 63

Phosphazene copolymers (Scheme 65) carrying nitrile, pyridine and phosphine ligands have been synthesized by sequential substitution from $[NPCl_2]_n$. Their reactions with $[W(MeOH)(CO)_5]$ gives the corresponding tungstencarbonyl complexes, that undergo a complete decarbonylation below 300 °C forming metal containing species that have a stabilizing effect on the polymeric matrices [252].



Scheme 65

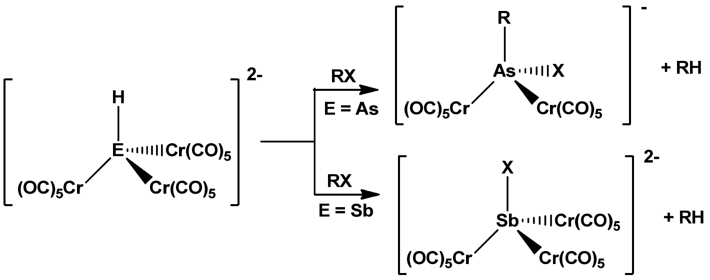
Polymer-bound ruthenium and molybdenum carbonyl fragments were prepared and their use in a ligand exchange reaction was demonstrated (Scheme 66) [253].



Scheme 66

In preparation of metal carbonyl anions: Gibson *et al.* generated group 6 metal carbonyl anions$HM(CO)_5^-$by Ion-Pair Extraction. Synthesis of$HM(CO)_5^-$(M = Cr or W) from $M(CO)_6$ utilizes tetraethylammonium hydrogen sulfate as the phase transfer aganet together with powdered KOH [254]. The reaction times were short and the product yields were good [255]. Cherng *et al.* have synthesized chromium pentacarbonyl derivatives of arsenic (V) and antimony (V) (Scheme 67) [256].

The tungsten and molybdenum hexacarbonyls, $M(CO)_6$ (M = W, Mo), dissolve in fluorosulfonic acid, HSO_3F, to generate the tungsten and molybdenum carbonyl cations, $[M(CO)_4]^{2+}$(solv), which are transformed, by exposure to an NO atmosphere, into the tungsten and molybdenum carbonyldinitrosyl cations, $[M(CO)(NO)_2]^{2+}$(solv), respectively (Scheme 68) [257].



Scheme 67

$$M(CO)_6 \xrightarrow[-2\,CO]{HSO_3F} [M(CO)_4]^{+2}(solv) \xrightarrow[-3\,CO]{+2\,NO} [M(CO)(NO)_2]^{+2}(solv)$$

Scheme 68

Mo(CO)$_4$(LL) complexes, where LL = polypyridyl ligands such as 2,2′-bipyridine and 1,10-phenanthroline, undergo quasi-reversible, one-electron oxidations in methylene chloride yielding the corresponding radical cations, [Mo(CO)$_4$(LL)]$^+$ (Figure 11). These electrogenerated species undergo rapid ligand substitution in the presence of acetonitrile, yielding [Mo(CO)$_3$(LL)(CH$_3$CN)]$^+$ [258].

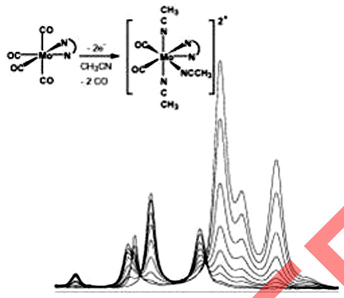


Figure 11. Generation of Metal carbonyl cations from Mo(CO)$_4$(LL) complexes, where LL =2,2′-bipyridine or1,10-phenanthroline [258].

The cationic alkoxy and hydroxycarbyne complexes [M$_2$Cp$_2$(μ-COR)(μ-PR'$_2$)$_2$]BF$_4$ (Cp = η^5-C$_5$H$_5$; M = W, R = Me, R' = Ph; M = Mo, R = Me and H, R' = Et) and [Mo$_2$Cp$_2$(μ-COR)(μ-COR')(μ-PCy$_2$)]BF$_4$ (R = Me; R' = H, Me, Et) are obtained in high yield by the reaction of the corresponding neutral monocarbonyl precursors with either [Me$_3$O]BF$_4$ or HBF$_4$·OEt$_2$ in dichloromethane [253-264].

6.5. Use of metal carbonyl complexes to achieve high enantioselectivity in the asymmetric allylboration of unsaturated aldehydes

The metal carbonyl units have been used as bulky substituents on chiral substrates enabling the diastereoselectivity of C-C bond forming reaction at adjacent positions to be enhanced [265]. The electronic and/or steric influence of the metal on the unsaturated organic ligand is of course central to the success of these and many other applications. William R Roush *et al.* report effect of metal carbonyl complexes, specifically the ability of such complexes to enhance the enantioselectivity of the asymmetric allylborations of unsaturated (aryl and propargylic) aldehydes. These reactions were in contrast to the previously reported examples in which the diastereoface selectivity of the metal carbonyl containing chiral substrates that is enhanced [265-275]. The reactions in which metal carbonyl ligand of achiral substrates lead to enhancement of the enantiofacial selectivity of a chiral reagent [276-278]. Previous studies have established that the asymmetric allylboration of aromatic aldehydes like benzaldehyde proceed with only moderate stereoselectivity of 55-72% in THF. The use of benzaldehyde chromium tricarbonyl complex as a surrogate for C$_6$H$_5$CHO [279], in the asymmetric allylboration with (*R,R*)-1 in toluene at -78 °C followed by oxidative decomposition provide (S) in greater than 90% yield. The (*E*)-crotylboration of chromium tricarbonyl complex with (*R,R*) was also provide 92% yield [280].

6.6. In preparation of catalysts

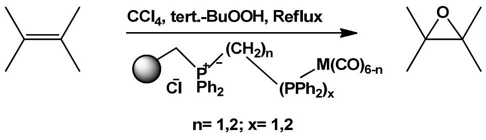
Cp*Mo(PMe$_3$)$_3$H undergoes carbonyl abstraction reactions with a variety of reagents, including CO$_2$, (CH$_2$O)$_n$, HCO$_2$H, and MeOH to yield Cp*Mo(PMe$_3$)$_2$(CO)H. The Cp*Mo(PMe$_3$)$_2$(CO)H serves as a catalyst for the decomposition of HCO$_2$H to CO$_2$ and H$_2$. [260] Preparation of alumina supported Pd-W and Pd-Mo catalysts was done photolytically from group VI metal carbonyls. Tungsten and molybdenum were introduced in γ-Al$_2$O$_3$ and Pd/γ-Al$_2$O$_3$ using metalcarbonyls [W(CO)$_6$ and Mo(CO)$_6$] photoactivation. The results showed that a reaction between the hexacarbonyls and the supported palladium particles takes place leading to bimetallic catalysts, with clear palladium-tungsten and palladium-molybdenum interactions (Scheme 69).

$$Pd + Mo(CO)_6 \xrightarrow{h\nu} Pd + Mo(CO)_{6-x} \longrightarrow Pd\text{-}Mo(CO)_{6-x} \xrightarrow{h\nu} Pd\text{-}Mo$$

Scheme 69

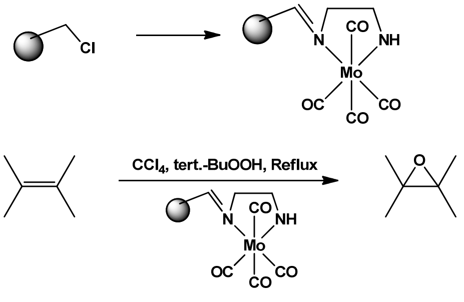
Both group VI metals strongly modify the chemisorption properties of palladium, while molybdenum seems to be present in a reduced state in close association with palladium [281].

Molybdenum carbonyl complexes immobilized onto polymer-bound phosphines were easily prepared in two steps from commercially available chloromethylated polystyrene resin. These catalysts were found to efficiently catalyze epoxidation of a wide variety of alkenes, including aromatic and aliphatic terminal alkenes using *tert*-butylhydroperoxide (Scheme 70). The new heterogenized molybdenum carbonyl epoxidation catalysts can be easily recovered by simple filtration and show no appreciable loss of activity even after 10 times of recycling. Hence they show a new class of novel reusable and highly active epoxidation catalysts [282].



Scheme 70

Polymer-bound Schiff base ligandwas prepared by oxidation of chloromethylated polystyrene to aldehydic polystyreneand then reaction with ethylene diamine. The functionalized polystyrene was used to immobilize $Mo(CO)_6$ and polymer-bound molybdenum carbonyl Schiff base catalystwas produced. This supported catalyst shows high activity in epoxidation of various alkenes in the presence of *tert*-butylhydroperoxide (Scheme 71). The supported molybdenum catalyst can be recovered and reused for eight times without loss in its activity [283].



Scheme 71

7. Studies done on metal carbonyl complexes

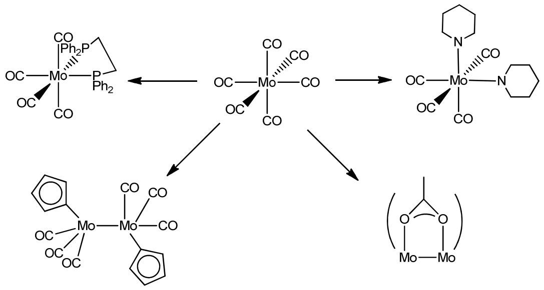
Kinetics and mechanism of CO substitution reaction of $M(CO)_6$ (M= Cr, Mo, W) with $(CH_3)_3NO$ in the absence and presence of triphenyl phosphine PPh_3 were incestigated. The rates of reaction are first-order in concentrations of $M(CO)_6$ and of $(CH_3)_3NO$ but zero-order in PPh_3 concentration. The rate of reaction decrease in the order W>Mo≈Cr. The mechanism was suggested with the formation of coordinatively unsaturated intermediates of the type $M(CO)_5$, which then rapidly react with an entering ligand [284].

Thermally activated ligand-dissociation processes in substituted group 6B metal carbonyl derivatives involving the tightly bound, ubiquitous phosphine or phosphate ligands have rarely been studied quantitatively. Kinetic and mechanistic studies of *cis*-$Mo(CO)_2L_2$ derivatieves (L = phosphine or phosphate) are presented for the substitution reaction of one of the ligands (L) by carbon monoxide. These processes were observed to proceed by a dissociative mechanism with the rate of substitution being greatly enhanced as the size of the phosphorus ligand increases within a series of phosphine or phosphate derivates. The *cis*-$Mo(CO)_4L_2$ species were found to react stereo specifically with CO to afford *cis*-$Mo(CO)_4L_2$ derivative was observed to be nonfluxional during its solution lifetime. Rate studies of phosphine dissociation in *trans*-$Mo(CO)_4(PPh_3)_2$ are reported which dekmonstrate this process to be less facile when compared with the analogous process in *cls*-$Mo(CO)_4(PPh_3)_2$ [285]. The enthalpies of (i) the dissociation reactions of the carbonyl ligand in $Cr(CO)_n$ [n = 6, 5, 4], $Fe(CO)_5$, and $Ni(CO)_n$ [n = 4, 3, 2], (ii) the dissociation reactions of the heteroligand L in $Cr(CO)_5L$ [L = CS, Xe, H_2, C_2H_4, C_2F_4], $Cr(CO)_3L$ [L = C_6H_6, C_6Me_6], and $Fe(CO)_4L$ [L = H_2, C_2H_4], (iii) the deprotonation reactions of $Cr(CO)_3C_6H_6$ and $Fe(CO)_3C_4H_6$, (iv) the protonation reaction of ferrocene, and (v) the hydrogenation reactions of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were calculated at the DFT/BP86, MP2, MP3, SCS-MP2, and SCS-MP3 levels and compared with the corresponding experimental data. It was found that the erratic behavior of the low-order MP approaches can be corrected by the newly developed spin component scaled (SCS) perturbation theory. The SCS-MP3 enthalpy of the hydrogenation reaction of $Mn_2(CO)_{10}$ (5.8 kcal/mol) agrees better with the experiment (8.7 ± 0. 3 kcal/mol) than the BP86 value (1.7 kcal/mol). The SCS-MP3 proton affinity of metal-protonated ferrocene (214.8 kcal/mol) and of the agostic form (203.9 kcal/mol) compare well with the experimental values (206–213 kcal/mol) and contrary to MP2 do not exclude the dynamic behavior of protonated ferrocene. It is suggested that for complex chemical systems including transition metals simultanous application of DFT and SCS-MP3 methods may be helpful to increase the reliability of the predictions [286].

Vaporization thermodynamics of low and high (>400 g/mol) molecular weight (MW) carbonyls were compared. A gravimetric-torsion effusion method was used to measure vapor pressures of carbonyls such $Os_3(CO)_{12}$, $Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$, $Co_2(CO)_8$, $Cr(CO)_6$, and $W(CO)_6$carbonyls. The studies found that $Os_3(CO)_{12}$, $Cr(CO)_6$, and $W(CO)_6$ have shown virtually no disproportionation in structure [287].

Dombek and Angelici done study of the reaction of group 6 metal thiocarbonyl complexes with nucleophiles. They found that primary amines readily react with $M(CO)_5(CS)$ complexes where (M = Cr, Mo, W) to give isocyanide complexes, $M(CO)_5(CNR)$. Secondary amines are found to give lower yields of thioformamide complexes $W(CO)_5(S{=}C(H)NR_2)$. Kinetic studies show a second order dependence in amine concentration. It was suggested that the rate-determining step is the addition of a hydrogen-bonded amine to the thiocarbonyl atom. The phosphine substituted analogues, cis- and trans-$W(CO)_4(CS)(PPh_3)$ reacts much slower, presumably due to increased electron density at the thiocarbonyl ligand. Azide ion reacts rapidly with $M(CO)_5(CS)$, forming cleanely the known $W(CO)_5(CS)$. A number of weaker nucleophiles including water, alcohols, hydrazine, aniline, ammonia, CH_3SH and Ph_3PO do not react with $W(CO)_5(CS)$. Stronger nucleophiles such as CH_3Li, R_2NLi and RO^- appear to add to the CS ligand, although the reactions are not straightforward [288].

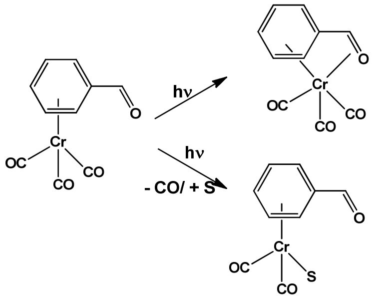
A range of microwave-enhanced reactions of group VIb metal carbonyls were presented by Ardon *et al.* (Scheme 72). Molybdenum hexacarbonyl is particularly well suited to this procedure, with reactions generally proceeding cleanly and without need for an inert atmosphere. Reactions of chromium and tungsten hexacarbonyls are less impressive [289].



Scheme 72

Many carbonyl diimine complexes of first-row transition metals have been found to be photoreactive under irradiation into their lowest metal-to-ligand charge-transfer (MLCT) absorption band (metal → α-diimine), the observed primary reaction corresponding to a carbonyl loss. Metal-to-ligand charge-transfer (MLCT) excited-state dynamics of $Cr(CO)_4(bpy)$ (bpy = 2,2‘-bipyridine) have been investigated through wave packet propagations on CASSCF/MR-CCI potentials and compared with the results of recent femtosecond time-resolved spectroscopic study [290].

Photoinduced CO-loss and arene-loss from $(\eta^6$-$C_6H_5Y)Cr(CO)_3$ (Y = NH_2, OCH_3, H, CHO or CO_2CH_3) result from discrete photophysical processes whose efficiency depends on the solvent (Scheme 73). The quantum yield (Φ) for arene loss is greater in halocarbon than in hydrocarbon solvents [291].



Scheme 73

Zhang *et al.* studied cyclopentadienylmolybdenum carbonyls $Cp_2Mo_2(CO)_n$ (Cp = η^5-C_5H_5; n = 6–1) (Figure 12) by density functional theory and predicted stability of metal carbonyl complexes [292]. The two lowest energy structures predicted for $Cp_2Mo_2(CO)_6$ lie within 4 kcal/mol of each other. Both have Mo–Mo single bonds of lengths 3. 2–3. 3 Å with all terminal carbonyl groups and correspond to stable compounds. Similarly, the lowest energy structure predicted for $Cp_2Mo_2(CO)_4$ has a formal Mo≡Mo triple bond of length ~2. 5 Å with four weakly semibridging carbonyl groups also corresponding to a stable compound structurally characterized by X-ray diffraction. The pentacarbonyl $Cp_2Mo_2(CO)_5$, which is not known experimentally as a stable compound but only as a transient intermediate, is shown to have a structure with one symmetrical bridging two-electron donor and four terminal carbonyl groups as well as a formal Mo=Mo double bond. Furthermore, $Cp_2Mo_2(CO)_5$ is predicted to be thermodynamically unstable with respect to disproportionation into $Cp_2Mo_2(CO)_6$ + $Cp_2Mo_2(CO)_4$. The lowest energy structure for $Cp_2Mo_2(CO)_3$ is a triplet with a formal Mo≡Mo triple bond. A higher energy singlet structure with one four-electron-donor bridging carbonyl group is also found for $Cp_2Mo_2(CO)_3$.

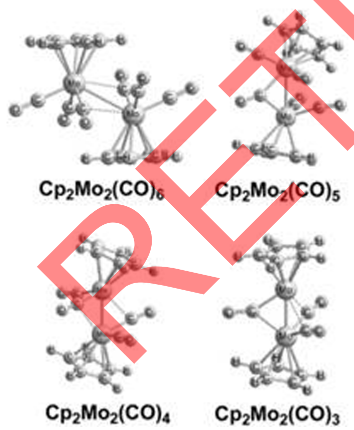


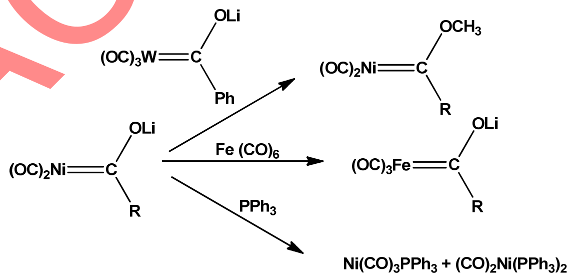
Figure 12. X-ray crystallogh of cyclopentadienylmolybdenum carbonyls $Cp_2Mo_2(CO)_n$ (Cp = η^5-C_5H_5; n = 6-1) [292].

Intramolecular carbonylcarbonyl interactions in W, Mo and Fe complexes containing the η^1-*N*-maleimidato ligand was found both for experimental and calculated structures. It is probably the first approach to explain this type of intramolecular interactions acting in organometallic compounds. The investigations indicate also the differences in the character of bonding between the η-*N*-maleimidato ligand and the central metal atom [293].

The adsorption and thermal behavior of (η^6-benzene)tricarbonyl chromium (0), (η^6-C_6H_6)Cr(CO)$_3$, inside zeolite Y have been investigated. The thermal decomposition of (η^6-C_6H_6)Cr(CO)$_3$ in zeolite Y seems strongly dependent on the experimental conditions employed: heating (η^6-C_6H_6)Cr(CO)$_3$ adsorbed inside zeolite Y in a Schlenk tube under nitrogen flow results in the formation of benzene and Cr metal, whereas heating the same complex in a closed vessel yields a different metal carbonyl species, $Cr(CO)_6$ [294].

The electronic description of octahedral (*fac*- $[M(CO)_3L_3]^n$, with M = Re, Ru, and Mn, and $[Cr(CO)_5L]^n$), square-planar (*cis*-$[Pt(CO)_2L_2]^n$), and tetrahedral ($[Ni(CO)_3L]^n$) carbonyl complexes (where L = monodentate ligand) was obtained. The analysis indicates that while ligand electronic parameters may be considered as a measure of the net donor power of the ligand, the net transfer of the electron density (or charge) does not occur from the ligand to the metal ion. In $[M(CO)_xL_y]^n$ carbonyl species, the charge transfer occurs from the ligand L to the oxygen atom of the bound carbon monoxides. This charge transfer translates into changes of the polarization (or permanent dipole) and the covalency of the C≡O bonds, and it is this effect that is probed in IR spectroscopy. As the analysis shifts from IR radiations to electrochemical potentials, the parameters best describe the relative thermodynamic stability of the oxidized and reduced $[M(CO)_xL_y]^{n/n+1}$ species. No relationship is found between the metal natural charge of the $[M(CO)_xL_y]^n$ fragments analyzed and the parameters [295].

The reactivity of a nucleophilic nickel acylate complex with a tungsten carbene complex, $Fe(CO)_5$, $Cr(CO)_6$, PPh_3, and CO was investigated. With the tungsten carbene complex, a methyl transfer occurred. With the metal carbonyl complexes, the acylate group on the nickel and a carbonyl on the iron or chromium traded places. With the PPh_3 and CO, the acylate anion was replaced by the phosphine or CO ligand (Scheme 74) [296].



Scheme 74

8. Conclusion

The G-VIb metal carbonyl complexes are of great interest toscientists since last 5 decades, and various studies have been done on these molecules. The successful development of metal carbonyl complexes and their products has been demonstrated by various examples of recent literature. The review article highlights various types of metal carbonyl complexes, complexation agents and substitution reactions of G-VIb metal carbonyls with various ligands. This review has given just a few examples of what is being done in the area as we change to our work of the future.

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