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CYCLOPENTADIENYL COMPLEXES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

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CONTENTS

1. INTRODUCTION

The considerable interest shown in the cyclopentadienyl complexes of the chromium triad is due in large measure to the wide variety of bonding and stereochemical situations which they present. Zero-valent chromium, molybdenum and tungsten require the donation of a total of twelve ligand electrons to achieve the configuration of the next inert gas and, as we shall see in the body of this review, this situation may be arrived at by coordination to virtually any appropriate combination of 1-, 2-, 3-, 4-, 5- or 6-electron ligands. The tendency of molybdenum and tungsten to achieve coordination numbers higher than six and to retain the π-bonded cyclopentadienyl ligand in complexes of high formal oxidation states is also of considerable importance.

The assignment of metal oxidation state in many of the complexes to be discussed is tenuous at best. The current literature would seem to favor regarding the π-bonded C_5H_5 group as $C_5H_5^-$, donating six electrons to the metal in question. Thus the complex h^5–$C_5H_5Mo(CO)_3Cl$ is regarded as containing Mo^{II} with the chloro ligand arbitrarily assigned as Cl^-, a two-electron donor. Similarly $[h^5$–$C_5H_5Cr(CO)_3]_2$ would be a Cr^I complex, diamagnetism being achieved by formation of the metal–metal bond. We will use such assignments with care, although this type of approach probably very nearly represents the true state of affairs in complexes such as h^5–$C_5H_5MoCl_4$.

Much of our attention will be directed to the cyclopentadienylmetal carbonyl derivatives of group VI. In particular we will concern ourselves with the structure, bonding and stereochemical aspects of the chemistry of these complexes. Leading references are supplied for instances in which parallels are known to exist in the behavior of low-valent compounds of other transition metals. We have attempted to make this review of the literature as comprehensive as possible through 1971.

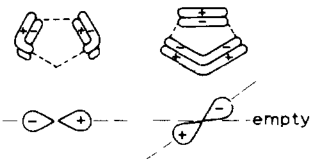
In the interest of clarity we have chosen to abbreviate C_5H_5 as Cp when the ligand is bonded to the metal via all of the ring carbons. Standard abbreviations of organic groups are similarly employed, e.g. Ph = C_6H_5, Me = CH_3, i-Pr = iso-C_3H_7.

II. STRUCTURE AND BONDING

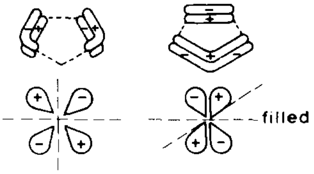
A. Description of metal–ligand bonding

Virtually all of the cyclopentadienyl complexes of the Group VI metals have structures in which the five carbon atoms of the ring lie in a plane approximately equidistant from the metal atom. The bonding in this situation consists of two interrelated electron donations. Electron density is transferred from the hydrocarbon ligand to the metal via overlap of filled ring MO's with vacant metal orbitals of appropriate symmetry. The resultant charge build-up at the metal atom may be compensated by retrodative bonding of filled metal orbitals with appropriate MO's of the ring system.

By analogy to the bonding scheme worked out by Schustorovich and Dyatkina[1] for ferrocene, the principal contributions to binding in cyclopentadienylmetal complexes may be pictorialized as shown below:



Forward bond

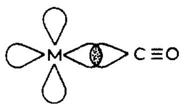


Back bond

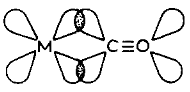
Charge is transferred to the metal by the overlaps indicated as the "forward bond" with the "back bond" removing electron density from the metal and donating charge to the ring. Other ligand–metal orbital interactions no doubt play a role in the overall bonding scheme but presumably are less important. We should reemphasize at this point that these conclusions are based on calculations for the highly symmetric ferrocene-type molecules and should not be rigorously applied to complexes of lower symmetry [2]. Nonetheless the gross features of metal–cyclopentadienyl bonding presented above serve as a reasonable approximation of the electronic interactions in these and related complexes.

Other π-ligands such as olefins and allyl systems can be bound simultaneously with the cyclopentadienyl ligand. The bonding of these ligands is generally described in similar fashion to that presented for the cyclopentadienyl moiety [3].

Bonds to carbon monoxide and related ligands involve a filled ligand orbital (in valence bond terminology, the carbon *sp* hybrid) overlapping a vacant metal orbital of proper symmetry. Multiple bond character is provided by back-donation from filled metal orbitals to the empty CO π-antibonding orbitals, although the detailed picture may not be as simple as this. This description predicts a weakening of the C–O bond relative to uncomplexed carbon monoxide, in accord with infrared studies of a variety of transition metal carbonyl complexes [4].



Forward bond



Back bond

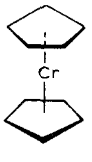
The multiple bonds formed by the cyclopentadienyl and carbon monoxide ligands and the charge delocalization implied thereby make the NMR shifts of the C_5H_5 protons and infrared C–O stretching frequencies of these complexes sensitive to changes in electron density at the metal atom. These features are considered in detail for specific complexes in Section IV.

Similar treatments effectively explain the bonding of trivalent phosphorus ligands, where vacant *d* orbitals are utilized to accept electrons from the metal. A more complex case is the nitrosyl ligand which is formally regarded as a 3-electron donor, generally forming linear metal–NO bonds. The 3-electron donation may be envisioned as complete transfer of one electron to the metal, the resulting nitrosonium ion being isoelectronic with carbon monoxide and bonding in similar fashion [5].

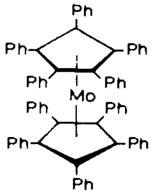
In complexes containing σ bonds between a Group VI metal and groups such as H, CH_3, Cl, $Si(CH_3)_3$ or another transition metal, the bonding is best represented from a valence bond point of view. These are more or less classical σ bonds in which the electron density lies about a line connecting the bonded nuclei.

B. Structures of representative complexes

Of the simple dicyclopentadienyls of Group VI only chromocene, Cp_2Cr, is known. The complex is isomorphous with ferrocene, presumably having the staggered structure (1) in the solid state [6]. In accordance with the bonding scheme for Cp_2M complexes[1] this compound has a magnetic moment of 3.2 BM, corresponding to two unpaired electrons. From cell dimension data the chromium carbon bond distance has been estimated as 2.2 Å[7]. Molybdenocene has recently been isolated but it appears to be polymeric and of uncertain structure at this time [8]. The reported properties of "molybdenocene" differ markedly from those reported earlier [9]. The reasons for this discrepancy are not clear at present. The complex Cp_2W has been postulated as a transient intermediate, but has not been isolated [10]. Decamethylmolybdenocene $[(CH_3)_5C_5]_2Mo$ is dimeric in solution [8], while decaphenylmolybdenocene (from the high pressure reaction of diphenylacetylene and $Mo(CO)_6$)[11] may have the structure (2).



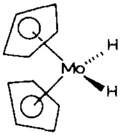
(1)



(2)

The decreasing tendency of $(R_5C_5)_2Mo$ complexes to polymerize as R varies from H to Me to Ph is most reasonably explained in terms of steric effects. Regarding the Cp ligand as occupying three coordination sites, Cp_2M complexes are formally six coordinate. The preference of the heavier transition elements on the left side of the periodic table for coordination numbers higher than six and for formal oxidation states higher than +2 are almost certainly important factors in the "nonexistence" of stable monomeric dicyclopentadienyls of Mo, W, Nb, Ta, Zr, and Hf.

The simplest dicyclopentadienyl complex of molybdenum is Cp_2MoH_2 (3) [12]. The ring–Mo–ring angle is 145° [13] but molecular orbital calculations[14] indicate that such distortion from parallelism should not result in loss of significant M–Cp bond energy. Cp_2WH_2 presumably has the same structure.



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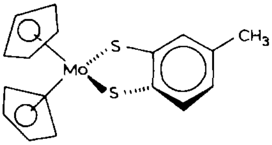
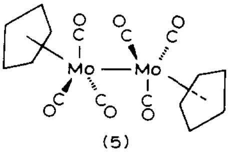


(4)

The toluene dithiolato complex (4)[15] has a similar structure [16]. The sulfur ligand is planar within experimental error, as are the Cp ligands. Principal differences from the dihydride (3) are the smaller (133°) angle between ring normals and the fact that the Cp ligands are staggered. The staggered configuration mimimizes CH–CH repulsions which would result from the eclipsed arrangement found in Cp_2MoH_2.

Complexes of the formula π-C_5H_5MXY(M = Mo, W and X, Y = Cl, Cl; C_6H_5, Cl; C_6H_5, H) are known[17] and probably have structures related to those of (3) and (4). Similarly, Cp_2WS_4 has the bent Cp–W–Cp conformation and contains a non-planar W–S_4 arrangement[18]. A recent study of the bonding in Cp_2MX_2 complexes[19] seems to give a better fit of observed/calculated angles than the earlier[14] model. Chromium analogs are unknown to date, presumably due to steric factors and limitations of oxidation state and coordination number.

The complex $[CpMo(CO)_3]_2$, an important starting material for the preparation of a wide variety of cyclopentadienylmolybdenum complexes, has the structure (5)[20]. Diamagnetism is achieved by formation of a Mo–Mo bond 3.22 Å in length. Half of this distance is frequently quoted in comparing calculated-found Mo–X distances in other structures. Infrared studies suggest that the chromium and tungsten complexes have similar structures. The absence of bridging carbonyls in all these species in noteworthy. Interesting examples of complexes which do contain bridging ligands are (6)[21] and (7)[22].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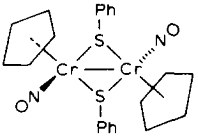
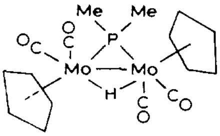
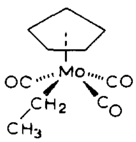

(6)


(7)

Infrared studies[23] have shown that the complexes $[CpMo(CO)_3]_2X^+$ (X = H, I) have a center of symmetry while $[CpMo(CO)_3]_2SnR_2$ derivatives (R = alkyl) have the expected bent Mo–Sn–Mo arrangement.

Considerable interest has been shown in cyclopentadienyl-molybdenum and -tungsten carbonyl alkyls. The driving force for these investigations is the need for accurately determined metal–carbon σ lengths. The earliest of these determinations was $CpMo(CO)_3Et$ (8)[24].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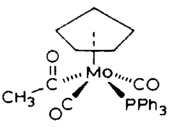
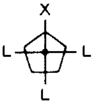

(9)

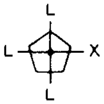
The Mo–C_α distance of 2.397 Å agrees well with the sum of the molybdenum covalent radius (from $[CpMo(CO)_3]_2$) and the carbon sp^3 radius. (The "piano-stool" geometry of these complexes is apparently a general feature of $CpML_3X$ complexes and should be borne in mind for later discussions.) The complex $CpMo(CO)_3C_3F_7$ has a Mo–$C(CF_2)$ distance of 2.288 Å, indicating metal-orbital contraction by the electronegative C_3F_7 group or backbonding to σ^* orbitals[25]. The fluoroalkyl derivative $CpMo(CO)_3C_3F_7$ has essentially the same geometry and bond angles as those noted for (8) as does the tungsten complex $CpW(CO)_3C_6H_5$ [26].

The complex $CpMo(CO)_2(PPh_3)COCH_3$[27] has been shown to have the structure (9)[28] in which the triphenylphosphine and acetyl groups are in the *trans* orientation.

The Mo–acetyl C distance is only 2.264 Å, indicating d_π–p_π back bonding to the acetyl group, represented in valence bond terms [27, 29] as $\mathrm{M{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH} \leftrightarrow \overset{+}{\mathrm{M}} = \mathrm{\overset{\displaystyle O^-}{\overset{|}{C}}{-}CH_3}$. The question of *cis–trans* isomerism in $CpM(CO)_2(L)X$ complexes is treated in more detail in Sections IV and V.

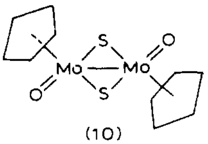
In Mo^{II} complexes of the general formula $CpMo(L)_3X$ the two orientations below are preferred in the solid state (viewing the molecule along the Mo–ring center axis). Virtually all of the complexes





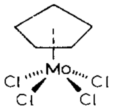
studied to date show a preference for the structure in which X (the σ-bonded group) passes directly under a ring carbon. Exceptions are $[CpFe(CO)_2]_2[CpMo(CO)_3]SnCl$ [30] and *cis*-$CpMo(CO)_2[P(n\text{-}Bu)_3]I$ [31]. Whether these differences are due to preferred bonding orientations or packing effects is not clear at present.

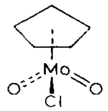
Up to this point we have mainly considered complexes in which the Group VI metal may be regarded as being in the 0 or +2 oxidation states and (with the exception of Cp_2Cr) obeying the effective atomic

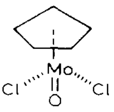


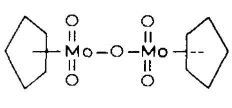
(10)

number rule. A large number of complexes are known which contain several oxygen, sulfur, or halogen ligands in addition to π-C_5H_5. The only complex of this type for which X-ray data are available is (10)[32]. The complex $[CpMoO_2]_2$ presumably has the same metal-ligand arrangements. Proposed structures for related compounds are shown below [33]:









C. Trends in the chromium triad

Although discussion of oxidation states in complexes of the type discussed here is tenuous, some generalizations can be put forward. The absence of chromium compounds with chromium in oxidation states higher than +3 is noteworthy. Halides and oxy-halides of molybdenum and tungsten in the IV, V and VI valence states are well characterized[34]. This apparent trend to greater stability of higher oxidation states in the heavier members of the group is consistent with the general behavior of the transition elements. The higher coordination numbers obtained in molybdenum and tungsten are similarly consistent with known trends and has been mentioned above to rationalize the "nonexistence" of Cp_2CrH_2 and related derivatives.

The consensus of physical and chemical evidence currently at hand suggests that tungsten forms stronger metal–carbon bonds than do molybdenum and chromium. The inertness to substitution of $W(CO)_6$ relative to $Mo(CO)_6$ and $Cr(CO)_6$ is well documented[35] and has been attributed to the lanthanide contraction affording an inordinately strong W–C bond[36]. The ease of replacement of carbonyl groups by the cyclopentadienide anion is consistent with this idea and appears to increase in the order $Cr(CO)_6 < W(CO)_6 < Mo(CO)_6$ [36]. The complexes $CpM(CO)_3R$ (R = Me, Et) are both thermally and oxidatively more stable for M = W, and the chromium analogs are incompletely characterized[37, 38].

Substitution of phosphines for CO in $CpM(CO)_3R$[26] or $CpM(CO)_3X$ (M = Mo, W)[39] requires more drastic conditions for the tungsten complexes than for molybdenum. Disubstituted derivatives $CpM(CO)L_2X$ were obtained only with M = Mo[39, 40] in thermal reactions.

As with all generalizations, this trend in M–C bond strength must be treated with caution. For example, the activation energies of the first order substitution reactions of $M(CO)_4(dipy)$ (dipy = 1, 1′-dipyridyl) with phosphites to yield $M(CO)_3(L)(dipy)$ are virtually independent of M[41]. The thermal substitutions of $CpM(CO)_2NO$ with triphenyl phosphine to afford $CpM(CO)(Ph_3P)NO$ [42] are more facile for molybdenum and tungsten than for chromium, although infrared data would suggest that, of the starting materials, the chromium compound has the weakest M–CO bonds. This anomaly could be due to a difference in mechanism for the Mo and W complexes, but to date a kinetic study of these reactions has not been reported.

There appears to be little doubt that the metal–metal bond in the complexes $[CpM(CO)_3]_2$ is weakest in the chromium complex. No species containing two chromium atoms is observed in the mass spectrum of $[CpCr(CO)_3]_2$; the corresponding molybdenum complex exhibits the ion $[Cp_2Mo_2]^+$ as the base peak in the spectrum [43, 44]. Chemical evidence to the same effect is the observation that $[CpCr(CO)_3]_2$ is cleaved to $CpCr(CO)_3H$ by molecular hydrogen, whereas this reaction does not occur with the molybdenum and tungsten complexes [45]. The stability of the hydrides $CpM(CO)_3H$ toward thermal or oxidative degradation decreases W>>Mo>Cr [37], paralleling the trends in M–C and M–M bond strengths cited above.

III. SYNTHESES OF SELECTED COMPOUNDS

In this section we will describe in some detail the syntheses of the more important cyclopentadienyl complexes of Group VI. Our definition of importance is based upon routes illustrating general procedures or routes leading to compounds which are in turn of synthetic utility in their own right. For a more general treatment of preparation of C_5H_5 metal complexes we recommend the review by Birmingham [46] and the text written by King [47].

A. Chromocene, Cp_2Cr

As with virtually all the dicyclopentadienyls of the first row transition metals the most convenient preparation of Cp_2Cr involves treatment of $CrCl_3$ (anhydrous) with sodium cyclopentadienide in tetrahydrofuran (THF) [48,49]. The reaction is carried out with vigorous

$$CrCl_3 + 3NaC_5H_5 \xrightarrow[25°,\,4h]{THF} (C_5H_5)_2Cr + 3NaCl + \{C_5H_5\}$$

exclusion of air. At the conclusion of the reaction solvent is removed at reduced pressure and the residue vacuum sublimed to afford approximately 60% yields of red crystals of the extremely air sensitive product, melting point 173°. A less desirable preparation involves $Cr(CO)_6$ and C_5H_6 at about 300° [50]. Chromocene may be treated with carbon monoxide under pressure to afford the difficultly accessible $[CpCr(CO)_3]_2$ [48].

B. Cp_2MoH_2 and Cp_2WH_2

These complexes are obtained in yields up to 50% by treatment of WCl_6 or $MoCl_5$ with excess sodium cyclopentadienide and sodium borohydride in THF solution [12]. The metal halide is added to the rest of the reaction mixture at 0° and the resultant slurry then refluxed four hours to ensure complete reaction. Solvent is removed at reduced pressure and the product sublimed at 120°/0.1 mm. All operations must be conducted under nitrogen or argon (that diborane is a by-product should be noted). The complexes Cp_2MH_2 are used as starting materials for the preparation of dicyclopentadienyl metal halides and related derivatives [17] (see Section IV).

C. $[CpM(CO)_3]_2$ (M = Cr, Mo, W)

The diversity found in the Group VI cyclopentadienyls is well illustrated by the syntheses of these dimeric complexes. The direct reaction of cyclopentadiene with $Cr(CO)_6$ affords Cp_2Cr [50], not the carbonyl dimer. The chromium complex is available via the high-pressure carbonylation of chromocene [48, 51].

$$Cp_2Cr + CO \xrightarrow[160°]{100\text{ atm}} [CpCr(CO)_3]_2 + \{C_5H_5\}$$

Attempts to prepare a cycloheptatrienyl chromium complex led inadvertently to what may well be the most convenient preparation of $[CpCr(CO)_3]_2$ [52]:

$$2CpCr(CO)_3^- Na^+ + 2C_7H_7Br \rightarrow [CpCr(CO)_3]_2 + C_{14}H_{14} + 2NaBr$$

King recommends the preparation of $[CpMo(CO)_3]_2$ by the direct thermal reaction of dicyclopentadiene and $Mo(CO)_6$ [47]. Yields from this reaction are variable and extremely unpredictable, however for reasons which are as yet unknown.

$$C_{10}H_{12} + Mo(CO)_6 \xrightarrow{135-145°} [CpMo(CO)_3]_2 + H_2$$

The method of the authors' choice involves intermediate synthesis and aerial oxidation of $CpMo(CO)_3H$ [37, 53]. Sodium cyclopentadienide and $Mo(CO)_6$ under nitrogen are refluxed in THF overnight. The reaction mixture is allowed to cool to room temperature and excess glacial acetic acid is added to form $CpMo(CO)_3H$.

$$NaC_5H_5 + Mo(CO)_6 \xrightarrow[\text{reflux}]{\text{THF}} Na^+[CpMo(CO)_3]^-$$

$$CpMo(CO)_3^- + H^+ \rightarrow CpMo(CO)_3H$$

$$CpMo(CO)_3H \xrightarrow[\text{(air)}]{0_2} [CpMo(CO)_3]_2 + H_2O$$

Air is bubbled slowly through the solution of the hydride for 3–5 hours forming the characteristic deep red color of the dimer. Solvent is removed at aspirator vacuum, the residue extracted with chloroform and filtered. Crystallization from chloroform/heptane and washing with pentane affords 75–80% yields of the product as a deep red violet solid, m.p. 216°. Product of higher purity may be obtained by sublimation at 160°/0.1 mm, but with considerable sacrifice in yield.

The synthesis of $[CpW(CO)_3]_2$ is best conducted by the thermal dicyclopentadiene/ $W(CO)_6$ route [47]. The hydride oxidation route outlined for molybdenum fails for as yet unexplained reasons.

The complexes $[CpM(CO)_3]_2$ are convenient starting materials for a variety of reactions as discussed in the next section. Their stability relative to many of the monomeric $CpM(CO)_3X$ (X = H, alkyl, halide) derivates is a consideration when dealing with large quantities of these complexes in a systematic study. The analogous π-indenyl complexes of molybdenum have been prepared by the thermal reaction of indene with molybdenum carbonyl [54, 55]. Chromium and tungsten analogs are not known to date.

D. Nitrosyl complexes

The diamagnetic chromium complex $CpCr(NO)_2Cl$ is prepared from chromium(III) chloride, sodium cyclopentadienide and NO [47, 56].

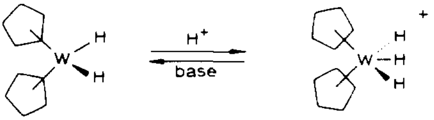
$CrCl_3 + NaC_5H_5 + 2NO \rightarrow CpCr(NO)_2Cl + NaCl + \{C_5H_5\}$

The reaction is carried out in THF and NO is added last, giving an exothermic reaction. The complex $[CpCrCl_2]_2$ is presumably an intermediate [56]. $CpCr(NO)_2Cl$ is a reasonably air stable green solid decomposing at 140° without melting. It may be converted to other $CpCr(NO)_2X$ derivatives by metathetical reactions and reacts with CH_3MgBr to afford $CpCr(NO)_2CH_3$ [37] which is more stable thermally than $CpCr(CO)_3CH_3$. Treatment of aqueous solutions of $CpCr(NO)_2Cl$ with sodium borohydride produces the dimeric $[CpCr(NO)_2]_2$ [57]. The complex $CpMo(NO)_2Cl$ is prepared by the reaction of $CpMo(CO)_3^-Na^+$ with excess $PhN_2^+Cl^-$, $NaNO_2$ and HCl [58]. The monomeric complexes $CpM(CO)_2NO$ are prepared in fair yield from $[CpCr(CO)_3]_2$ or $CpM(CO)_3^-$ (M = Mo, W) and nitric oxide [59–62]. An improved synthesis of $CpMo(CO)_2NO$ involves treatment of $CpMo(CO)_3^-Na^+$ with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide [63].

IV. REACTIONS

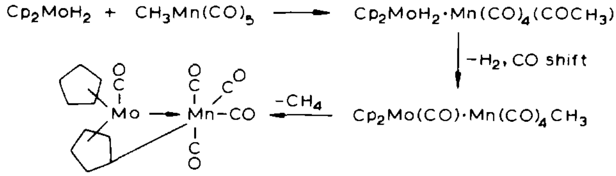
A. Cp_2MH_2 (M = Mo, W)

As mentioned in Section II these complexes have structures in which the C_5H_5 rings are canted with the angle between the ring normals being approximately 145°. An additional structural feature of these complexes is the presence of a "sterically active" lone pair of electrons, whose presence is indicated by molecular orbital calculations [14, 19] as well as chemical properties. Thus Cp_2WH_2 is reversibly protonated [12] to afford a trihydride cation which gives

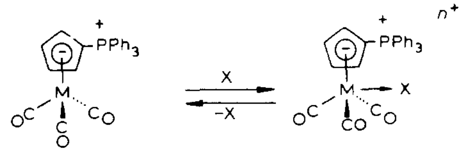


rise to an A_2B proton NMR pattern in the metal hydride region (~16 ppm upfield from TMS). This nonequivalence of the protons bonded to the metal indicates that the canted structure is retained in the protonated complex. Similar structures are presumably involved [64, 65] in Cp_2FeH^+ [66], Cp_2ReH [67], Cp_2TeH [68], Cp_2TaH_3 [12] and the recently reported Cp_2NbH_3 [69].

The basicity of these complexes is not restricted to reaction with the proton. Thus Cp_2WH_2 forms reasonably strong Lewis acid–base adducts with BF_3 [70] and $Al(CH_3)_3$ [71]. One of the most intriguing examples of this behavior is the reaction of Cp_2MoH_2 or Cp_2WH_2 with $CH_3Mn(CO)_5$, which apparently proceeds as shown below [72]. The crystal structure of the $Cp_2MoH_2/CH_3Mn(CO)_5$ product has been determined. Reactions of Cp_2ReH and Cp_2TaH_3 proceed in similar fashion [72]. It seems likely that further examples of syntheses involving these complexes as ligands will be reported in the future. Finally, it should be noted that the related complexes $Ph_3PC_5H_4M(CO)_3$ [73] (M = Cr, Mo, W) undergo



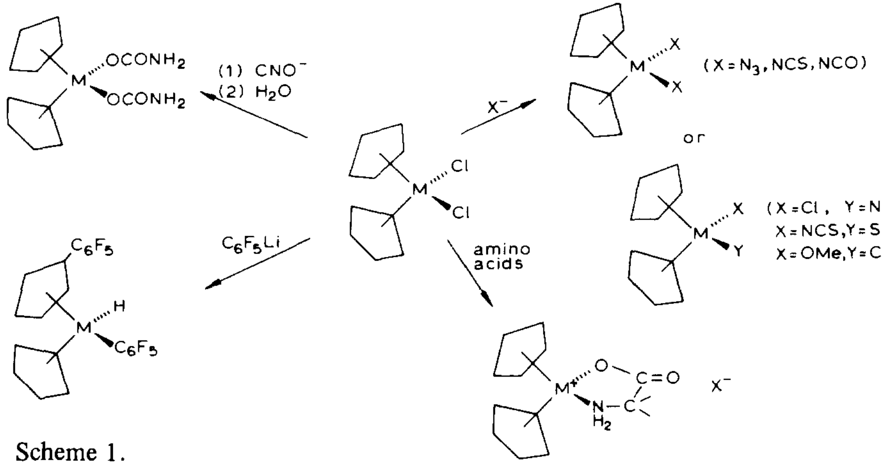
acid–base reactions with the metal as the basic center [74].



($n = 0$, X = BF ; $n = 1$, X = H^+)

Insertion reactions of Cp_2MH_2(M = Mo, W) acetylenes have also been reported. The "inserting" reagents bear electron-withdrawing substituents (CF_3, CO_2R) and it seems likely that these reactions are also due at least in part to the basicity of the metal atom [10, 75]. To our knowledge catalytic properties of these hydrides have not been reported to date, though this would seem a potentially fruitful area for future research *.

The complexes Cp_2MX_2 (synthesized from Cp_2MH_2) undergo a variety of substitution reactions in which the halide is displaced as X^- by pseudo-halides, nitrogen or sulfur ligands, or perfluoroaryl groups. These are summarized in scheme 1 [15, 17, 76].



Scheme 1.

Nitric acid oxidation of many of the Cp_2MXY complexes afford paramagnetic d^1 cations $[Cp_2MXY]^+$, isolated as hexafluorophosphate salts. These have been studied by electron spin resonance spectroscopy. Protonation of $Cp_2W(OR)CN$ (R = CH_3, C_2H_5) yield the "iso" hydrogen cyanide complexes $Cp_2W(OR)(CNH)^+$ [17]. The cation $[Cp_2Mo(SMe_2)Br]^+$ [77] reacts with a variety of primary amines to afford

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* *Note added in proof.* Results pertinent to catalyhe activity of these complexes have recently appeared. (A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 94 (1972) 1886).

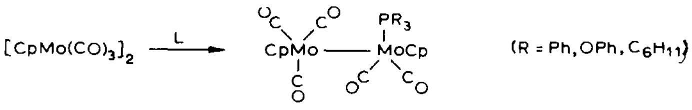
$[Cp_2Mo(NH_2R)H]^+$ complexes with concomitant oxidation of the amines to aldehydes or ketones [78]. Reactions of the tungsten analogs proceed similarly but require much more vigorous conditions [78]. The complexes Cp_2MoCl_2 (M = Mo, W) react with β-diketones to form ionic complexes of the type $Cp_2MoL^+X^-$ (L = diketone enolate)[78a].

The compounds $Cp_2M(SR)_2$ (M = Mo, W; R = alkyl or phenyl) may function as bidentate ligands, forming *cis*-$LM(CO)_4$ complexes (L = $Cp_2W(SR)_2$; M = Cr, Mo or W) [79] by reaction with Group VI hexacarbonyls. Reactions with $PdCl_2$ and $[\pi\text{-}C_3H_5RhCl_2]_2$ afford L_2Pd^{2+} and $[LRh^-\pi\text{-}C_3H_5]^+$ respectively [80].

B. $[CpM(CO)_3]_2$

The cyclopentadienylmetal carbonyls of chromium, molybdenum and tungsten are convenient starting materials for the production of a variety of derivatives $CpM(CO)_3X$ (X = H, alkyl, or a halogen) whose chemistry is discussed later in this Section. Substitution and other reactions of the $[CpM(CO)_3]_2$ complexes have been restricted mainly to molybdenum, presumably due to the difficulty in synthesizing the chromium complex [48, 52] and the low reactivity exhibited by $[CpW(CO)_3]_2$ [27, 40, 81].

Triphenylphosphine substitution of CO to afford $Cp_2Mo_2(CO)_5PPh_3$ occurs readily in refluxing tetrahydrofuran or hexane [27]. Ultraviolet irradation of hexane [27] or benzene [82] solutions of these reactants proceeds similarly but in lower yields. Tricyclohexylphosphine and triphenylphosphite behave similarly [82, 83]. When excess PPh_3 is employed in the photochemical reaction, formation of the ionic $[CpMo(CO)_2(PPh_3)_2]^+[CpMo(CO)_3]^-$ becom the dominant process [82]. Ionic products of the formula $[CpMo(CO)_2(L)_2][CpMo(CO)_3]$ are the only isolable substitution products when the entering ligand is PEt_3 [82], PBu_3 [83] or 1, 2-bis(diphenylphosphino)ethane (diphos) [82, 84]. These observations suggest that phosphine basicity enhances heterolytic Mo–Mo bond cleavage. The reaction path taken by diphos is not readily explained in terms of basicity, and closure of the ligand to form the chelated product would seem to be the logical driving force in this case. When $[CpMo(CO)_3]_2$ is photolyzed with excess $P(OPh)_3$ or $P(OBu)_3$ in benzene neutral, symmetrically substituted complexes of the formula $[CpMo(CO)_2L]_2$ are produced [82, 83]. The corresponding PPh_3 complex may be prepared by heating $[CpMo(CO)_2(PPh_3)_2]CpMo(CO)_3$ in vacuo at 160° [82].

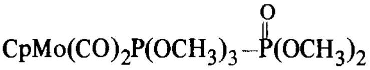


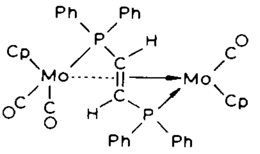
$$[CpMo(CO)_3]_2 \xrightarrow[h\nu]{L} [CpMo(CO)_2(L)_2][CpMo(CO)_3]$$

The difficulty encountered in substituting the second ligand into $Cp_2Mo_2(CO)_5L$ probably is a reflection of steric factors. However, substitution at one molybdenum atom could alter the electron density (and thence Mo–CO bond strength) at the second metal and electronic effects are not to be completely ignored.

The nature of the disubstituted complex isolated utilizing forcing conditions is a function of the nature of the phosphorus ligand employed as well as reaction conditions [85, 86]. Refluxing benzene as solvent affords the ionic products $[CpMo(CO)_2L_2]^+CpMo(CO)_3^-$ while UV irradiation leads to the complexes $[CpMo(CO)_2L]_2$, L = a tertiary phosphine or phosphite. The thermal reaction appears to proceed via the intermediate $Cp_2Mo_2(CO)_5L$ [86]. The detailed mechanism of this process is not known, but an S_N2 type attack of the second phosphorus ligand at the already crowded molybdenum appears unlikely. In the photochemical process $Cp_2Mo_2(CO)_5L$ is presumably formed also but successive excitation, loss of CO, and capture of L apparently compete favorably with the heterolytic Mo–Mo bond cleavage.

These processes are analogous to the reactions of $Mn_2(CO)_{10} + 2L_2$ and $Co_2(CO)_8 + 2L$ (both ionic and covalent products depending upon L, temperature, and solvent) [87].

If L is a phosphite, phosphonite or phosphinite, still another type of product may be isolated, e.g.  $CpMo(CO)_2P(OCH_3)_3-\overset{\overset{O}{\|}}{P}(OCH_3)_2$ from $[Cp_2Mo(CO)_3]_2$ and trimethylphosphite. These products have been rationalized in terms of a Michaelis–Arbuzov type rearrangement assisted by the metal [86]. *Trans*–$Ph_2PCH = CHPPh_2$ undergoes a photochemically assisted reaction with $[CpMo(CO)_3]_2$ affording a novel complex which has been assigned the structure shown below on the basis of IR and NMR spectroscopic evidence [88].



Infrared and proton NMR spectra for representative complexes are shown in Table 1. Substitution of a carbonyl group by a phosphorus ligand (weaker π-acceptor) increases back donation to both the remaining carbonyl groups and the cyclopentadienyl ligand [89]. This is demonstrated by the shifts of $\nu(CO)$ to lower frequencies and the C_5H_5 resonances to higher fields. As we shall see in subsequent discussions this is a general feature of these and related cyclopentadienylmetal carbonyl derivatives.

As noted in previous sections $[CpMo(CO)_3]_2$ undergoes a variety of oxidation and oxychlorination reactions in which the Mo–Cp bond remains intact [33] and $[CpCr(CO)_3]_2$ reacts with nitric oxide to form $CpCr(CO)_2NO$ [59]. $[CpMo(CO)_3]_2$ is an effective catalyst for the addition of CCl_4 and carbon monoxide to a variety of olefins [90].

C. CpM(CO)$_2$NO and CpM(NO)$_2$Cl

The chemistry of these complexes has apparently not been studied extensively. This

TABLE 1

Compound	*ν(CO)*[a]	*δ(C₅H₅)* [b,c]	*Reference*
$[CpMo(CO)_3]_2$	1965 s, 1920 vs br	5.39(1)	27
$Cp_2Mo(CO)_5PPh_3$	1972 vs, 1895 vs, 1820 s	5.11(1) 4.72(2) *J*(PH) 1.5 Hz	27,82
$Cp_2Mo_2(CO)_5[P(OPh)_3]$	1976 ms, 1891 br 1816 m	——	82
$[CpMo(CO)_2PPh_3]_2$	1853(sh), 1830 s	——	82
$\{CpMo(CO)_2[P(O{-}n{-}Bu)_3]\}_2$	1851 s	5.17(2) *J*(PH) 1.2 Hz	82
$\{CpMo(CO)_2[P(OC_3H_5)_3]\}_2$	1866 m , 1844 s	4.90(2) *J*(PH) 1.7 Hz	86

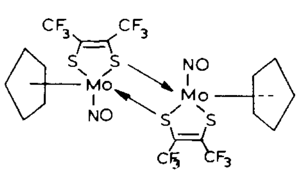
[a] Dichloromethane or chloroform solutions.
[b] ppm downfield from internal tetramethylsilane.
[c] Multiplicity in parentheses; 1 = singlet, 2 = doublet.

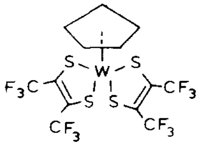
may be due in part to the difficulty of their preparation, but is nevertheless surprising in view of the fact that they are isoelectronic and isostructural with cyclopentadienylmanganese tricarbonyl (cymantrene) which has been the subject of a considerable number of investigations [3, 91, 92]. At least one parallel with cymantrene chemistry is known: the Friedel–Crafts acetylation of $CpCr(CO)_2NO$ to afford $(CH_3COC_5H_4)Cr(CO)_2NO$ [56].

The substitution reactions of the $CpM(CO)_2NO$ complexes with triphenylphosphine illustrate dramatically the metal–CO bond strength variation mentioned in Section II [42]. Thus the complex $CpMo(CO)(PPh_3)NO$ is obtained by refluxing the dicarbonyl nitrosyl with excess ligand in benzene. The corresponding tungsten complex is also accessible thermally but refluxing toluene is required for the reaction to proceed at a convenient rate. The thermally inaccessible $CpCr(PPh_3)_2NO$ and $CpMo(PPh_3)_2NO$ are obtained by ultraviolet irradiation, but the corresponding.tungsten complex could not be isolated even under these conditions. Diphos ($Ph_2PCH_2CH_2PPh_2$) reacts thermally with $CpMo(CO)_2NO$ to yield CpMo(diphos)NO. Presumably the proximity of the second phosphorus atom and a chelation effect account for the differences in behavior between diphos and triphenylphosphine. Further studies of the photochemical reactions of these complexes with triphenylphosphine led to the isolation and characterization by X-ray crystallography of $CpM(CO)(PPh_3)_2NCO$ [93]. The intermediacy of a molybdenum nitrene complex was suggested to account for this novel result.

The complexes CpM(CO)(NO)(L) should be optically active, but have not been resolved into pure enantiomers. Their optical activity has been demonstrated, however, by means of proton NMR spectroscopy [94] with the complex $CpMo(CO)(NO)(PMe_2Ph)$. The methyl groups of the phosphorus ligand are magnetically non-equivalent due to the asymmetry at the molybdenum atom. Similar observations were reported for related complexes of iron, manganese and cobalt [94].

The complex $CpMo(CO)_2NO$ reacts with bis(trifluoromethyl) dithietene to afford the diamagnetic $[C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2$ while the corresponding reaction with tungsten affords the paramagnetic $C_5H_5W[S_2(CF_3)_2]_2$





which is readily reduced to the uninegative ion having the inert gas configuration [63]. The molybdenum maleonitriledithiolate complex $CpMo(S_2C_2CN_2)_2{}^-PPh_4{}^+$ has the metal ligand arrangement shown above for the neutral tungsten complex [95]. $CpMo(CO)_2NO$ reacts with iodine to form $[CpMo(NO)I_2]_2$, having two bridging iodide ligands [61]. Reactions of this complex with mercaptans or mercaptide anions afford the complexes $[CpMo(NO)(I)(SR)_2]_2$, $[CpMo(NO)(SR)]_2$ and $[CpMo(NO(SR)_2]_2$ depending upon the reaction conditions [96]. All of these compounds have been assigned structures containing bridging ligands on the basis of infrared, NMR and mass spectral data. $[CpMo(NO)I_2]_2$ reacts with phosphorus or nitrogen donor ligands to form monomeric complexes of the formula $CpMo(NO)I_2L$ ($L = PPh_3, P(OPh)_3$, py) [61].

Metathetical reactions of $CpCr(NO)_2Cl$ with anions seem to constitute the entire known chemistry of this class of compounds. Sodium borohydride produces the dimeric $[CpCr(NO)_2]_2$ [5] with $CpCr(NO)_2H$ presumably formed as an unstable intermediate. Reactions of $CpCr(NO)_2Cl$ with CH_3MgBr, $AgSCF_3$ and $LiNMe_2$ afford $CpCr(NO)_2CH_3$ [37], $CpCr(NO)_2SCF_3$ [97] and $[CpCr(NO)(NMe_2)]_2$ [98], respectively. An X-ray investigation of $CpCr(NO)_2NCO$ has shown it to have the expected "piano-stool" geometry [98].

D. CpM(CO)$_3$X

Substitution of carbon monoxide or halogen in the derivatives $CpMo(CO)_3X$ ($X = Cl$, Br or I) has been accomplished with a variety of donor ligands. The tungsten complex $CpW(CO)_3Cl$ has been studied less extensively and no work has been reported on chromium analogs. The substitution reactions of metal carbonyls and metal carbonyl halides are the subject of two recent review articles [87, 99].

The product isolated from the thermal substitution reaction of individual $CpM(CO)_3X$ derivatives depends upon the basicity and π-acceptor ability of the entering ligand, the particular halide and the central metal. Thus $CpMo(CO)_3Cl$ reacts with ammonia or hydrazine to afford strictly the ionic derivatives $CpMo(CO)_3am^+X^-$ ($am = NH_3$ or N_2H_4) [100]. Under similar conditions (refluxing benzene) triphenylphosphine and $CpMo(CO)_3Cl$ yield only the covalent products $CpMo(CO)_2(PPh_3)Cl$ and $CpMo(CO)(PPh_3)_2Cl$ [39]. These differences reflect the greatly disparate abilities of the nitrogen and phosphorus ligands to backbond to the metal. With the corresponding bromides or iodides or with triphenylarsine or -stibine as the entering ligand only covalent monosubstituted products $CpMo(CO)_2(L)X$ are obtained thermally [39, 101, 102].

The tungsten complex $CpW(CO)_3Cl$ reacts with triphenyl- and triethylphosphines to afford $CpW(CO)_2(PPh_3)Cl$ and a mixture of $CpW(CO)_2(PEt_3)Cl$ and $CpW(CO)_2(PEt_3)_2^+Cl^-$ respectively [103]. The absence of covalent disubstituted products $CpW(CO)(L)_2Cl$ in these reactions is probably due to the differences in Mo–CO and W–CO bond strengths. The isolation of the ionic product $CpW(CO)_2(L)_2^+Cl^-$ for PEt_3 and not for PPh_3 reflects differences in basicity and π-acceptor ability of the phosphines. A disubstituted tungsten derivative has been obtained by the route below [34]:

$$CpW(CO)_3Cl \xrightarrow[CH_2Cl_2]{Cl_2} CpW(CO)_2Cl_3$$

$$CpW(CO)_2Cl_3 \xrightarrow{PPh_3} CpW(CO)(PPh_3)_2Cl$$

Although the mechanism of this reaction is not known, it seems likely that $CpW(CO)(PPh_3)Cl_3$ is an intermediate and that the reductive elimination of Cl_2 promotes the entry of the second phosphorous ligand.

Covalent substitution products involving 1,2-bis(diphenylphosphino)ethane (diphos) are consistent with the above results in terms of the number of carbonyl groups displaced. From $CpMo(CO)_3Cl$ and diphos the product $CpMo(CO)(diphos)Cl$ is isolated in low yield. From the analogous reaction of $CpMo(CO)_3I$ or $CpW(CO)_3Cl$ the only uncharged product obtained ($[CpM(CO)_2X]_2$-μ-diphos) had the bifunctional phosphine bridging two metals; no monocarbonyl species was found among the products [39].

In addition to the relatively small quantities of the above substances, the major product formed in each reaction of diphos is the ionic $CpM(CO)_2(diphos)^+X^-$. This result is most interesting since the thermal reactions with triphenylphosphine did not give analogous products [39]. One must recall nonetheless that the ionic compounds $CpM(CO)_2[(C_2H_5)_3P]_2^+Cl^-$ are major products of the reactions of $CpMo(CO)_3Cl$ or $CpW(CO)_3Cl$ and triethylphosphine [103]. One possible explanation for these results with triethyl- and triphenylphosphine involves the relative back-bonding capability of these ligands. Since reaction with a ligand with less back-bonding ability (viz., NH_3) apparently favors displacement of the halide ion rather than a carbonyl group, one might predict that alkylphosphines would be more likely to give the ionic product. Still, the extent of the differences between the reactions of diphos and those of triphenylphosphine is surprising if interpreted solely on this basis. It seems likely that the chelating ability and lower steric requirements of the diphos ligand may be in some way involved also. The formation of all of the products of the diphos reactions may be explained as arising from intermediate species of the type $CpM(CO)_2(diphos)X$ in which one of the phosphorus atoms remains uncoordinated. This type of intermediate has been observed in the reactions of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ with diphos [104].

$$\mathrm{CpM(CO)_2(diphos)X} \longrightarrow \mathrm{CpM(CO)(diphos)X + CO}$$

$$\mathrm{CpM(CO)_2(diphos)X} \longrightarrow \mathrm{CpM(CO)_2(diphos)^+X^-}$$

$$\mathrm{CpM(CO)_2(diphos)X + CpM(CO)_3X} \longrightarrow \mathrm{[CpM(CO)_2X]_2}\text{–}\mu\text{–}\mathrm{diphos + CO}$$

The chelating nitrogen ligands bipy and *o*-phen react rapidly with each of the cyclopentadienylmetal tricarbonyl halides to give exclusively the ionic products $\mathrm{CpM(CO)_2(bipy)^+X^-}$ and $\mathrm{CpM(CO)_2(\mathit{o}\text{-}phen)^+X^-}$. No covalent derivatives were formed in these reactions [39]. Pyridine and $\mathrm{CpM(CO)_3Cl}$ (M = Mo, W) gave no ionic product using reaction conditions similar to those employed in the above reactions. Small amounts of an unstable covalent derivative were sometimes observed, but this material could not be isolated [40]. The difference between bipy and pyridine also suggests that the chelating ability of the ligand may be the predominant factor in the formation of an ionic species. The failure of these nitrogen donor ligands to form stable covalent substitution products is most likely a consequence of their relatively poor π-acceptor capabilities.

Photochemical substitutions of $\mathrm{CpMo(CO)_3Cl}$ and $\mathrm{CpMo(CO)_3I}$ with a variety of Group VA donor ligands lead to product distributions significantly different from those observed in the thermal processes [105]. Irradiation promotes the formation of the ionic species $\mathrm{CpMo(CO)_2(L)_2{}^+X^-}$ where L = $\mathrm{PEt_3}$ *, $\mathrm{PPh_3}$, or $\mathrm{L_2}$ = diphos and the disubstituted neutral complexes $\mathrm{CpMo(CO)(L)_2Cl}$, L = $\mathrm{PEt_3}$, $\mathrm{AsPh_3}$, or $\mathrm{SbPh_3}$and $\mathrm{CpMo(CO)(L)_2I}$, L = $\mathrm{PEt_3}$, $\mathrm{P(OPh)_3}$, $\mathrm{AsMePh_2}$, $\mathrm{SbPh_3}$ or $\mathrm{L_2}$ = diphos, diars. Similar observations have been reported independently for chelating phosphorus ligands such as diphos [106].

A wide variety of cationic species of the type $\mathrm{[CpM(CO)}_n\mathrm{(L)}_{4-n}]^+\mathrm{X}^-$ has been prepared by means of the $\mathrm{AlCl_3}$-assisted removal of halide in the presence of the appropriate ligand [39, 105, 107–109]. These complexes react with a variety of nucleophilic agents to afford neutral complexes in which the entering nucleophile is added either at one of the coordinated ligands or at the metal [87, 110]. A particularly striking example of this behavior is the apparent reduction of a terminal carbonyl by sodium borohydride in the transformation $\mathrm{CpMo(CO)_3PPh_3{}^+} \rightarrow \mathrm{CpMo(CO)_2(PPh_3)CH_3}$ [110].

Neutral and cationic isocyanide complexes have been reported and serve to illustrate some of the variations mentioned above. The thermal reactions of $\mathrm{CpMo(CO)_3Cl}$ and $\mathrm{CpMo(CO)_3I}$ with phenyl isocyanide yield $\mathrm{CpMo(PhNC)_3Cl}$ and $\mathrm{CpMo(CO)_2(CNPh)I}$ as the sole products of the respective reactions [111]. The tendency of the chloride ligand to promote multiple substitution has been mentioned previously, but the neutral trisubstituted product in this instance has no parallel in the reactions of other ligands. This observation is consistent with the high π-acceptor abilities of isocyanides but is unexpected on steric grounds. That only monosubstitution occurs with the iodide emphasizes the extremely delicate balance of electronic and steric factors determining the product distributions in these systems.

The cyanide ion reacts with $\mathrm{CpMo(CO)_3Cl}$ and $\mathrm{CpW(CO)_3Cl}$ to yield

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* This complex is also the product of the thermal reaction as in the case of the W analog cited above.

$K^+[CpMo(CO)_2(CN)_2]^-$ and $CpW(CO)_3CN$ respectively [112], once again illustrating the reluctance of the tungsten complex to undergo substitution. Methylation (by treatment with MeI) affords the methyl isocyanide complexes $CpMo(CO)_2(CNCH_3)_2{}^+I^-$ and $CpW(CO)_3(CNCH_3)^+I^-$ in high yield. Reactions of $CpM(CO)_3Cl$ (M = Mo or W) with $R_2C{=}NLi$ afford complexes of the formula $CpM(CO)_2N{=}CR_2$ (R = Ph, t-Bu) or $CpM(CO)_2(Ph_2CNCPh_2)$, the latter containing an aza-allyl linkage [113–115]. The compound $CpMo(CO)_2N{=}CPh_2$ (presumably containing a multiple M–N bond) dimerizes with loss of CO to form $[CpMo(CO)N{=}CPh_2]_2$ [113].

Nucleophilic reactions of sulfur containing ligands have also been studied. Thus $CpMo(CO)_3Cl$ reacts with dialkyldithiocarbamates to form $CpMo(CO)_2S_2CNR_2$ (R = Me, Et) in which both sulfur atoms are coordinated to the metal [116]. $CpW(CO)_3Cl$ reacts with NaSMe yielding $CpW(CO)_3SMe$, which dimerizes upon irradiation to form the sulfur-bridged $[CpW(CO)_2SMe]_2$ [117].

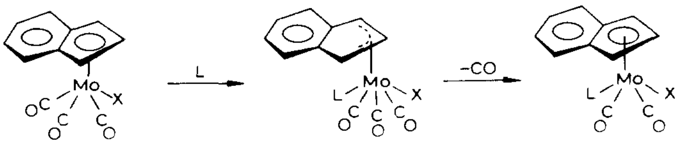
A kinetic study of the thermal substitution reactions of $CpMo(CO)_3X$ (X = Cl, Br, I) with a variety of phosphorus ligands has been reported [118, 119]. The formation of the monosubstituted complexes $CpMo(CO)_2(L)X$ is dissociative in nature, similar to the behavior of $Mn(CO)_5X$ [120]. The rates of the molybdenum reactions decrease Cl>Br>I, paralleling increases in ΔH^*. As expected for a dissociative

$$CpMo(CO)_3X \xrightarrow{\text{slow}} CpMo(CO)_2X + CO$$

$$CpMo(CO)_2X + L \xrightarrow{\text{fast}} CpMo(CO)_2(L)X$$

mechanism in which bond-breaking in the starting material is the dominant factor, the ΔS^*'s are positive and the rates correlated with M–CO bond strengths as indicated by ν(C–O) in the $CpMo(CO)_3X$ derivatives. The substitution reactions of $CpFe(CO)_2X$ also proceed via a dissociative mechanism [121]. Thus the observation that the cyclopentadienyl ligand promotes an associative S_N2 reaction in substitutions of $CpRh(CO)_2$ [122] is not a general phenomenon. Rather the nature of the metal and other attached ligands as well as coordination number are of considerable importance.

The importance of these factors has been elegantly demonstrated by kinetic studies of the indenyl [123] and tetrahydroindenyl [124] complexes $C_9H_7Mo(CO)_3$ and $C_9H_{11}Mo(CO)_3X$. These complexes retain the π-C_5H_5–Mo linkage but differ considerably in steric and electronic properties from their π-C_5H_5 analogs. The indenyl complexes exhibit a two-term rate law, $k_{obs} = k_A = k_B[L]$, and the k_A term is approximately 6000 times greater at 10° than for the corresponding C_5H_5 complexes. The latter effect is apparently due to stabilization of the "unsaturated" $C_9H_7Mo(CO)_2X$ intermediate by coordination of the six-membered ring of the indenyl ligand. The appearance of the second order path for the indenyl com-



plexes has been rationalized in terms of a "slippage" of the indenyl ligand in the transition state [123], allowing the metal atom to maintain both the inert gas configuration and constant coordination number. The saturated tetrahydroindenyl complex $C_9H_{11}Mo(CO)_3Cl$ exhibits kinetic parameters essentially identical to the cyclopentadienyl complex and no ligand-dependent path is observed [124].

Two other observations arising from these kinetic studies are worthy of special mention. In the reaction of $CpMo(CO)_3Cl$ with $P(n\text{-}Bu)_3$, $L_3Mo(CO)_3$ and $L_2Mo(CO)_4$ are major products. The C_5H_5 ligand is the leaving group in this case and departs as $[C_5H_5P(n{-}Bu)_3]^+$ presumably due to nucleophilic attack at cyclopentadienyl carbon. Nucleophilic attack at the metal with subsequent migration to the C_5H_5 ring cannot be ruled out, however [124]. Also, the uncertainty [54, 125] as to the structure of $C_9H_7Mo(CO)_2I$ appears to have been resolved. On the basis of infrared, mass spectral and X-ray data, the complex should be reformulated as the expected $C_9H_7Mo(CO)_3I$ [125]. The dicarbonyl complex was reported to be diamagnetic, presumably by virtue of bridging iodide ligands, but solution molecular weights were consistent only with a monomeric species [54]. Distinction between the dicarbonyl and tricarbonyl species on the basis of elemental analysis is not possible, as calculated values differ by less than one percent for all elements.

The infrared and proton NMR data of representative complexes are given in Table 2. These data afford insight into the bonding and electron distribution in these species, as substitution of CO by a ligand of different σ-donor and π-acceptor properties should result in a change in back-bonding to both the C_5H_5 and remaining carbon monoxide ligands [4, 89]. Considering the complexes $CpMo(CO)_3Cl$, $CpMo(CO)_2(L)Cl$ and $CpMo(CO)(L)_2Cl$ ($L = PPh_3$, $AsPh_3$, $SbPh_3$), it is apparent that substitution increases back-donation to both CO and Cp ligands systematically with increasing degree of substition. (Alternatively, these trends may reflect decreased donation by Cp and CO as a result of increased electron density at the metal). Atlhough these trends are predominantly electronic in nature, steric effects may be of some importance. The nature of the halogen appears to have little effect on $\nu(CO)$ or the C_5H_5 proton chemical shifts. These quantities are also remarkably similar for the triphenylphosphine, -arsine and -stibine derivatives considering the different back-bonding abilities usually ascribed to these ligands. A notable exception is the trend in $\delta(C_5H_5)$ for the $CpMo(CO)(L)_2Cl$ derivatives, consistent with the accepted π-acceptor trend $PPh_3 > AsPh_3 > SbPh_3$. Considerable variation in both $\nu(CO)$ and $\delta(C_5H_5)$ is noted in the substituted phosphine and phosphite complexes, indicating that substituents on the donor atom are more important than differences between phosphorus, arsenic and antimony. Small but real differences are noted between Mo and W derivatives bearing the same ligands, but these are not readily explained.

The derivatives $CpM(CO)_2(L)X$, due to their ' piano-stool" geometry can exist as *cis* or *trans* isomers. Consulting Table 2 it is seen that some of the complexes exhibit two C_5H_5 resonances, one a singlet, the other a doublet. This is recognized as being indicative of *cis* and *trans* isomers respectively [102, 126, 127]. The nature of L and X obviously exhibit considerable influence on the ratios of these isomers isolated from substitution reactions,

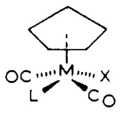
TABLE 2

Compound	*ν(CO)* [a]	*δ(C_5H_5) (ppm)* [b]	*Reference*
$CpMo(CO)_3Cl$	2040, 1940	5.62	40
$CpMo(CO)_2(PPh_3)Cl$	1975, 1885	5.41	39
$CpMo(CO)_2[P(OPh)_3]Cl$	1996, 1919	5.08	128
$CpMo(CO)_2[P\text{-}n\text{-}Bu_3]Cl$	1977, 1884	5.36	126, 118
$CpMo(CO)_2[P(OMe)_3]Cl$	1987, 1904	5.53, 5.39 (2)	128
$CpMo(CO)_2(AsPh_3)Cl$	1975, 1886	5.62	39, 105
$CpMo(CO)_2(SbPh_3)Cl$	1974, 1884	5.69	39, 105
$CpMo(CO)(PPh_3)_2Cl$	1795	4.88	40, 105
$CpMo(CO)(AsPh_3)_2Cl$	1791	5.05	105
$CpMo(CO)(SbPh_3)_2Cl$	1796	5.39	105
$CpMo(CO)_2(PPh_3)Br$	1980, 1890	5.37	39, 40
$CpMo(CO)_2(AsPh_3)Br$	1978, 1890	5.40	39, 40
$CpMo(CO)_2(SbPh_3)Br$	1980, 1889	5.41	39, 40
$CpMo(CO)_2(PPh_3)I$	1972, 1890	5.34, 5.11 (2)	40, 105
$CpMo(CO)_2[P(OPh)_3]I$	1992, 1918		105
$CpMo(CO)_2[P(C_6H_{11})_3]I$	1956, 1874	5.48	105
$CpMo(CO)_2(AsPh_3)I$	1966, 1883	5.60	105
$CpMo(CO)_2(SbPh_3)I$	1964, 1880	5.59	105
$CpW(CO)_2(PPh_3)Cl$	1965, 1872	5.56	40
$CpW(CO)_2(AsPh_3)Cl$	1962, 1870	5.39	40
$CpW(CO)_2(SbPh_3)Cl$	1965, 1870		40
$CpW(CO)_2[P(OMe)_3]Cl$	1972, 1884	5.67, 5.48 (2)	128
$CpW(CO)_2[P(OMe)_3]Br$		5.62, 5.47 (2)	128
$CpW(CO)_2[P(OMe)_3]I$	1972, 1890	5.60, 5.45 (2)	128
$CpW(CO)(PPh_3)_2Cl$	1780	5.02	34

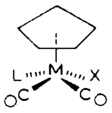
[a] Solution spectra.

[b] Relative to internal tetramethylsilane.

[c] Singlets unless otherwise noted. (2) = doublet, $J_{(PH)}$ 1.0–1.5 Hz.



trans



cis

although the reasons for these effects are not entirely understood at present. Further consideration is given to this point in Section V, where the dynamics of the *cis–trans* interconversion is discussed.

E. CpM(CO)₃R

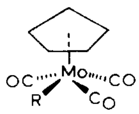
Few areas of transition metal organometallic chemistry have received the attention devoted to reactions involving formation and cleavage of the metal–carbon σ bond. This intense interest is due largely to the importance of such processes in catalytic reactions. The discovery in 1957 of the so-called carbon monoxide insertion reaction of $MeMn(CO)_5$ to afford $Me\overset{\overset{O}{\|}}{C}Mn(CO)_5$ marked the beginning of the systematic study of such processes [129]. Subsequent investigations have shown this type of behavior to be a general phenomenon, encompassing a wide variety of "inserting" reagents and metals [130, 131]. Catalytic implications of these reactions have been the subject of several excellent reviews [132–134].

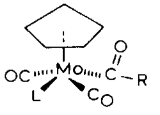
As mentioned previously $CpCr(CO)_3CH_3$ is the only known chromium alkyl of this general type and is thermally unstable. Its chemistry has not been studied in detail. A variety of $CpM(CO)_3R$ complexes (M = Mo, W, R = alkyl or aryl) is known and their chemistry has been extensively investigated. We will have occasion to note repeatedly, however, that considerable differences in behavior are encountered between tungsten and the other two metals due to the relatively great strengths of the W–CO and W–R bonds.

Among the first reactions of the $CpM(CO)_3R$ complexes noted is their decomposition to the dimers $[CpM(CO)_3]_2$ [135]. Exceptions are encountered in the decompostion of $CpMo(CO)_3Et$ [135] and $CpM(CO)_3Ph$ [136] (M = Mo, W) in which migration of the ethyl or phenyl groups to the cyclopentadienyl ring affords $[EtC_5H_4Mo(CO)_3]_2$ and $[PhC_5H_4M(CO)_3]_2$, respectively. The σ-allyl compound $CpMo(CO)_3CH_2CH{=}CH_2$ undergoes photochemical decarbonylation to form the corresponding π-allyl complex [137]. Protonation of the σ-allyl affords a cationic π-propylene complex. The complex $CpMo(CO)_3Et$ undergoes hydride abstraction to afford $CpMo(CO)_3(\pi\text{-}C_2H_4)^+$. This reaction is reversible, as $NaBH_4$ reduction of the ethylene cation regenerates the starting ethyl complex [137].

The earliest report of carbon monoxide "insertion" in the Group VI alkyls was the high pressure synthesis of $CpMo(CO)_3COEt$ from the ethyl derivative $CpMo(CO)_3Et$ [135]. This propionyl derivative is thermally unstable, a property extending to all known $CpM(CO)_3$ acyl complexes except those containing perfluoroalkyl groups [138].

In sharp contrast, the complexes $CpMo(CO)_2(L)COR$ [L = a tertiary phosphine or phosphite; R = Me, Et, allyl, benzyl] are thermally and oxidatively quite stable, being readily prepared from $CpMo(CO)_3R$ and the appropriate ligand in a variety of organic solvents [27, 139–144].

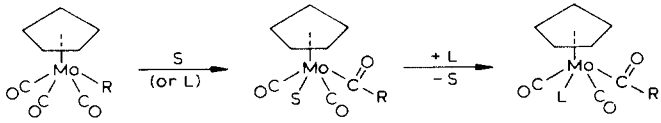




Proton NMR and infrared measurements indicate that these complexes exist predominantly as the *trans* isomers in solution, and the complex $CpMo(CO)_2(PPh_3)COCH_3$ has been shown by an X-ray investigation to have this geometry in the solid state [28]. It should be noted that the only substituted acyl complexes of tungsten reported to date do not result from this type of reaction. $CpW(CO)_2(PEt_3)COCH_3$ is produced from $CpW(CO)_3CH_3$ in neat PEt_3 at 50° [139] and traces of $CpW(CO)_2(PPh_3)COCH_3$ result from the reaction of $CpW(CO)_3COCH_3$ and PPh_3 in THF [40].

Kinetic studies of these reactions have shown them to be first order in molybdenum complex and independent of the nature of the ligand or its concentration [141–143]. A second order term appears in the rate expression only for nonpolar solvents and strongly nucleophilic phosphines [141].

The corresponding reactions of (π-indenyl) $Mo(CO)_3CH_3$ are considerably more rapid, presumably due to the ability of the indenyl ligand to "slip" and accommodate the incoming nucleophile [145]. First order rate constants as a function of solvent decrease in the order $CH_3CN > THF > DMF >$ toluene > hexane [141–143]. The nature of the alkyl group is also important, the rates in acetonitrile solvent decreasing $Et > Me > PhCH_2 >$ $> CH_2{=}CH{-}CH_2$. This has been interpreted to indicate little or no charge separation in the activated complex [143]. The proposed mechanism of these reactions involves a solvent (or ligand) assisted migration of the alkyl group to one of the terminal carbonyl groups, similar to the well-established routes in related manganese [146] and cobalt [147] systems. Whether the formation of the *trans* product is the result of kinetic [142] or thermodynamic [148] control is the subject of current debate [148] and is at this time an open question.

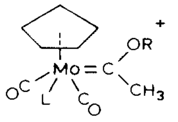


Chelating phosphines (e.g. diphos) afford acetyl complexes of the same general type with the phosphorus ligand bridging two or more metal atoms [27, 149, 150].

$$CpMo(CO)_3CH_3 + Ph_2PCH_2CH_2PPh_2 \rightarrow [CpMo(CO)_2COCH_3]_2\text{-}\mu\text{-diphos}$$

$$CpMo(CO)_3CH_3 + (Ph_2PCH_2CH_2)_2PPh \rightarrow [CpMo(CO)_2COCH_3]_3\text{-}\mu\text{-triphos}$$

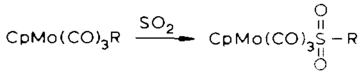
The complex $CpMo(CO)_2[P(hex)_3]COCH_3$ (hex = cyclohexyl) is converted into cationic "carbene" complexes by treatment with acid or onium salts [151].



(R = H, Et
L = $P(C_6H_{11})_3$)

The acetyl complexes *trans*-$CpMo(CO)_2(L)COCH_3$ [L = PPh_3, $P(OPh)_3$, $P(OMe)_3$, $P(n\text{-}Bu)_3$, $P(C_6H_{11})_3$] are decarbonylated stereospecifically to the corresponding *trans*-$CpMo(CO)_2(L)CH_3$ derivatives in a variety of solvents [144, 152]. The mechanistic details responsible for this stereoselectivity are not clear at present. Another feature of these decarbonylations is their dependence on the nature of L. The rates decrease $P(C_6H_{11})_3 > > PPh_2i\text{-}Pr > PPh_3 > PPh_2Me > P(n\text{-}Bu)_3PPhMe_2$ suggesting that steric, rather than electronic factors are important [152].

A variety of other reagents have been found to activate the Mo–R or W–R bond. Sulfur dioxide reacts readily with $CpMo(CO)_3R$ complexes (R = Me, Et, benzyl) to yield yellow crystalline *S*-sulfinate derivatives [153]. These reactions are much more facile than the corresponding reactions with CO.



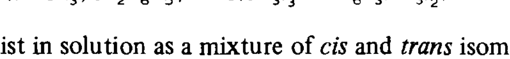
$$CpMo(CO)_3R \xrightarrow{SO_2} CpMo(CO)_3\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-R$$

The complex $CpMo(CO)_2(PPh_3)CH_3$ undergoes SO_2 insertion almost instantaneously at room temperature to afford $CpMo(CO)_2(PPh_3)\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-CH_3$.

The tungsten complexes $CpW(CO)_3CH_3$ and $CpW(CO)_3CH_2Ph$ are much less reactive toward SO_2 than their molybdenum counterparts [153]. The original report [27] that $CpMo(CO)_2(L)CH_3$ does not undergo reaction with CO has been found to be erroneous [154]. The reaction proceeds in a variety of solvents, predominantly by the route below [154].

$$CpMo(CO)_2(L)CH_3 \xrightarrow{CO} CpMo(CO)_3CH_3 + L \longrightarrow CpMo(CO)_2(L)COCH_3$$

The reactions of $CpMo(CO)_3CH_3$ and $CpMo(CO)_3CH_2C_6H_4X$ (X = *p*-H, *p*-Cl, *p*-OMe) with isocyanides yield different types of products, depending upon both the nature of the alkyl group on molybdenum and the isocyanide. With $CpMo(CO)_3CH_3$ or $CpMo(CO)_3CH_2C_6H_5$ and either t-butyl- or 2,6-dimethylphenyl isocyanide, insertion reactions analogous to those observed with phosphorus ligands occur [155]. These complexes

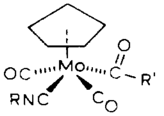


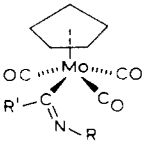
$$CpMo(CO)_3R + CNR' \longrightarrow CpMo(CO)_2(CNR')\overset{\overset{O}{\|}}{C}-R$$

($R = CH_3, CH_2C_6H_5$; $R' = C(CH_3)_3$ or $C_6H_3(CH_3)_2$)

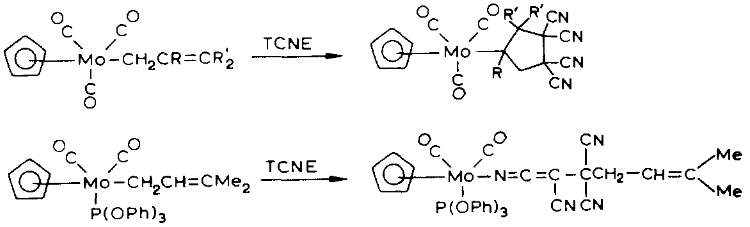
exist in solution as a mixture of *cis* and *trans* isomers. Decarbonylation of $CpMo(CO)_2[CNC(CH_3)_3]COCH_2C_6H_5$ affords only *trans*-$CpMo(CO)_2[CNC(CH_3)_3]CH_2C_6H_5$, again paralleling the behavior of the phosphine-substituted acyls.

With cyclohexyl isocyanide and CpMo(CO)$_3$CH$_3$ the substituted acyl-CpMo(CO)$_2$(L)COCH$_3$ is isolated as a mixture of *cis* and *trans* isomers (two C$_5$H$_5$ and two CH$_3$ proton NMR signals) [156]. Chloro- or cyanomethyl derivatives failed to react under similar conditions. The corresponding reactions with benzyl or substituted benzyl complexes gave both acyl and imino complexes arising from insertion of carbon monoxide and isocyanide, respectively [156]. The yield of imino complex relative to acyl complex decreases as a function of the *para*-substituent in the benzyl group, Cl > H > OMe. These studies demonstrate the delicate balance of steric and electronic controls possible in insertion reactions, as well as the extreme versatility of the isocyanide reagents.





Tetracyanoethylene (TCNE) has been shown to undergo related reactions with the molybdenum complexes CpMo(CO)$_3$CH$_2$CR=CR$'_2$ (R = H, R$'$ = Me; R = Me, R$'$ = H) and CpMo(CO)$_2$P(OPh)$_3$CH$_2$CH=CMe$_2$, affording 1,3- and 1,4-addition products respectively[15 This difference in behavior has been ascribed to the bulk of the phosphite ligand. CpMo(CO)$_2$(PPh$_3$)CH$_3$ is reported to behave similarly, but little detail was given[158].



The derivative CpMo(CO)$_3$CF$_3$ undergoes photochemical substitution of CO by triphenylphosphine to afford the perfluoromethyl derivative CpMo(CO)$_2$(PPh$_3$)CF$_3$ [159]. The absence of a perfluoroacetyl product is noteworthy and has been interpreted in terms of the relatively great strength of metal–CF$_3$ bonds compared to metal–CH$_3$ [160]. Preparation of CpMo(CO)$_2$(PPh$_3$) COCF$_3$ by other methods would allow examination of the rote of photochemical decarbonylation; a rapid rate of decarbonylation would explain the absence of perfluoroacetyl compounds in this substitution reaction. Experiments with the corresponding iron complexes CpFe(CO)(PPh$_3$)COCF$_3$ do not support this idea, however, but the molybdenum system is yet to be examined.

σ-Bonded aryl derivatives of the Group VI metals have not been studied extensively. Although CpW(CO)$_3$Ph is a stable entity, its chemistry has not been studied[136]. The corresponding molybdenum derivative is thermally unstable with the Mo–Ph bond undergoing spontaneous homolytic cleavage [136]. The complex CpMo(CO)$_2$(PPh)$_3$Ph has been prepared from CpMo(CO)$_2$(PPh$_3$)$^-$Na$^+$ and Ph$_2$I$^+$BF$_4$$^-$ and CpMo(CO)$_2$(PPh$_3$)I + + Ph$_2$Hg [161]. The benzoyl derivative CpMo(CO)$_2$(PPh$_3$)COPh [from CpMo(CO)$_2$(PPh$_3$)$^-$Na$^+$ and benzoyl chloride] is decarbonylated to the phenyl derivative by Rh(PPh$_3$)$_3$Cl [161]. Once again the thermal and oxidative stability conveyed by replacement of a CO ligand by a tertiary phosphine should be pointed out.

Many of the reactions described above have close parallels with the chemistry of $CpFe(CO)_2R$ derivatives [29, 162–167]. An exception is the stability of $CpFe(CO)_2Ph$ and its reaction with $P(OPh)_3$ to form $CpFe(CO)(P(OPh)_3)COPh$ and $CpFe(CO)(P(OPh)_3)Ph$ [167].

In Table 3 are presented infrared and proton NMR data for some of the complexes discussed above. These data clearly show that substitution of a phosphine for CO increases electron density at the metal atom, as the C_5H_5 chemical shifts are displaced to higher field and C–O stretching frequencies are lowered. Due to the irregular geometry of $CpM(CO)_2(L)R$ complexes and varying steric requirements of L, comparisons of σ-donor and π-acceptor abilities of the phosphorus ligands on the basis of these data probably should be avoided. In addition it cannot be stated with certainty whether the spectral differences observed are dominated by changes in electron acceptance or donation by the C_5H_5, CO and acyl groups. Both factors are important and cannot be readily separated, although this has been attempted with considerable success in complexes of higher symmetry [4].

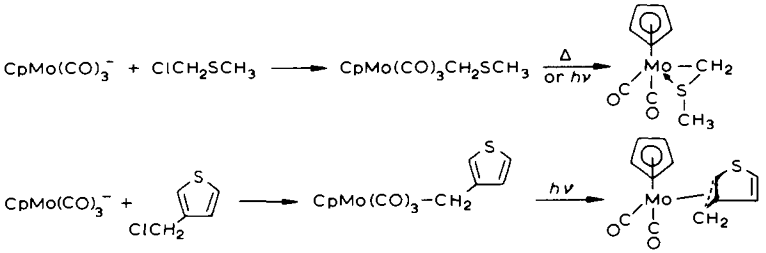
Several interesting alkyl and allyl complexes have been described which do not readily fit into the format we have chosen, but which are analogous to complexes discussed above.

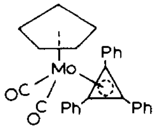
TABLE 3

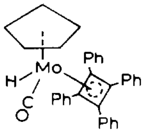
Compound	*$\delta(C_5H_5)$* [a, b]	*$\nu(CO)(cm^{-1})$*	*$\nu(COCH_3)(cm^{-1})$*	*Reference*
$CpMo(CO)_3CH_3$	5.28	2020 1937 1932		139
$CpMo(CO)_3COCH_3$	5.51	2015 1935(br)	1627	40
$CpMo(CO)_2(PPh_3)COCH_3$	4.99 (2)	1943 1858	1603	142
$CpMo(CO)_2(PPh_3)CH_3$	4.70 (2)	1940 1850		27, 144
$CpMo(CO)_2\{P(n\text{-}Bu)_3\}COCH_3$	5.00 (2)	1936 1847	1602	142
$CpW(CO)_2(PPh_3)CH_3$	4.73 (2)	1930 1845		27
$CpW(CO)_2(PEt_3)COCH_3$	5.17 (2)	1927 1847	1614	139
$CpMo(CO)_2[P(OCH_2)_3CMe]COCH_3$	5.21 (2)	1983 1878	1618	142

[a] Values in $CDCl_3$ solvent, chemical shifts in ppm downfield from internal TMS.
[b] (2) = doublet, J(PH) 1.0–2.0 Hz

The reaction of Na[CpMo(CO)$_3$] with ClCH$_2$SCH$_3$ affords the σ-alkyl complex CpMo(CO)$_3$CH$_2$SCH$_3$ which may be thermally or photochemically decarbonylated to afford CpMo(CO)$_2$CH$_2$SCH$_3$ [168]. The latter complex is isoelectronic with and formally analogous to π-allyl derivatives, as shown by an X-ray diffraction study [169]. A similar route to the π-thenyl derivative shown above has been described [170]. The latter complex is noteworthy as the three carbons of the π-allyl linkage are derived from the exocyclic methylene group and two ring carbons. Further complexes containing π-ligands in addition to the Cp group are the triphenylcyclopropenyl [171] and tetraphenylcyclobutadiene [172] derivatives:







King has recently reported the synthesis of pentamethylcyclopentadienyl complexes of the formula (π-Me$_5$C$_5$)M(CO)$_3$CH$_3$ (M = Mo, W) by the reaction of Me$_5$C$_5$COCH$_3$ with Mo(CO)$_6$ and (CH$_3$CN)$_3$W(CO)$_3$ respectively [173]. The acetyl derivatives (π-Me$_5$C$_5$)M(CO)$_3$COCH$_3$ presumably are intermediates in these reactions but decarbonylate under the reaction conditions [173]. In addition the complexes [(π-Me$_5$C$_5$)M(CO)$_2$]$_2$ are isolated (M = Cr, Mo) in which a metal–metal triple bond[174] is presumed to be present, accounting for the diamagnetism of compounds.

The chemistry of the hydride complexes CpM(CO)$_3$H has not been studied extensively, although they are employed as in situ reagents for the generation of halide derivatives and the dimeric [CpMo(CO)$_3$]$_2$. CpMo(CO)$_3$H undergoes insertion of C$_2$F$_4$ affording the tetrafluoroethyl complex CpMo(CO)$_3$CF$_2$CF$_2$H [175, 176]. The corresponding reactions of ethylene or CpM(CO)$_3$H (M = Cr, W) have not been reported. Hydrogenation of polyenes by CpM(CO)$_3$H occurs readily, with unstable CpM(CO)$_3$R complexes as presumed intermediates. When M = Mo or W, the reactions are stoichiometric with [CpM(CO)$_3$]$_2$ being formed essentially quantitatively [177]. This reaction is catalytic if CpCr(CO)$_3$H is employed [178]. These differences as a function of the metal employed are explained by the ability of [CpCr(CO)$_3$]$_2$ to react with hydrogen, regenerating the active metal hydride [177]. This reaction does not occur with the molybdenum and tungsten dimers, and a catalytic cycle cannot be established.

The complexes CpM(CO)$_3$H (M = Mo, W) react directly with a variety of phosphines and phosphites in acetonitrile at room temperature to afford $CpM(CO)_2(L)H$ derivatives [179]. These complexes were assigned *cis* stereochemistry on the basis of proton NMR spectroscopy, but a subsequent investigation [126] disclosed that they actually exist as a mixture of *cis* and *trans* isomers over a wide range of temperatures. (See Section V for further discussion on this point.)

F. Complexes with metal–metal bonds

A considerable number of complexes containing the $CpM(CO)_3$ group bonded to a second metal carbonyl via a metal–metal bond are known [3, 180] but will not be discussed in detail here. These complexes are generally prepared by reaction of the appropriate $CpM(CO)_3^-$ sodium salt and the carbonyl halide of the second metal, e.g. $NaCpW(CO)_3$ + + $Mn(CO)_5Cl \rightarrow CpW(CO)_3Mn(CO)_5 + NaCl$ [181]. Studies of these complexes have been limited mainly to their synthesis and spectral characterization.

The complexes $[CpM(CO)_3]_2Hg$ [47, 51] are of considerable interest due to their utility in the synthesis of complexes unavailable or obtained in low yield from other routes. Thus $[CpMo(CO)_3]_2Hg$ reacts with a variety of phosphorus ligands to afford complexes of the formulas $[CpMo(CO)_2(L)]_2Hg$ [126, 128] or $[CpMo(CO)_2L]Hg[CpMo(CO)L_2]$ [182]. These complexes may be cleaved by halogen to form $CpMo(CO)_2(L)X$, $CpMo(CO)_2(L)HgX$ or $CpMo(CO)L_2X$ derivatives. Sodium amalgam cleavage of these compounds generates $[CpMo(CO)_nL_{3-n}]^-Na^+$ which react with alkyl halides or main group metal halides to generate alkyls or new metal–metal bonded derivatives [126, 128, 182]. Similar utilization of $[CpCr(CO)_3]_2Hg$ and $[CpW(CO)_3]_2Hg$ [183] has led to the synthesis of new halide complexes of these metals. The chromium derivatives $CpCr(CO)_3X$ and $CpCr(CO)_2LX$ [X = Br, I; L = PPh_3, $P(OMe)_3$] are considerably less stable than their molybdenum counterparts [183]. The related complexes $[CpM(CO)_3]_2Cd$ (M = Mo, W) have been reported to undergo reactions with $CdBr_2$ and CdI_2 yielding $CpM(CO)_3CdX$ [184]. The compounds $[CpM(CO)_3]_2Zn$ are dissociated in solution, dissociation increasing Cr > Mo > W [185].

Few complexes containing bonds to Group III metals are known to date. The reaction of CpTl with $Mo(CO)_6$ leads surprisingly to the formation of $Tl[CpMo(CO)_3]_3$ rather than $Tl[CpMo(CO)_3]$ [186]. The nature of the bonding in this complex is uncertain. Treatment of $CpMo(CO)_2(L)H$ (L = CO or a phosphine) with alkylaluminums or dialkylaluminum hydrides affords $R_2Al{-}Mo(CO)_2(L)Cp$ compounds which contain a very reactive Mo–Al bond [187]. The complex $Al[CpW(CO)_3]_3 \cdot 3THF$ [188] has been shown to contain octahedral aluminum, with the $CpW(CO)_3$ groups each coordinated to aluminum by a carbonyl oxygen. In solution the complex shows the reactivity expected of the $CpW(CO)_3^-$ ion.

The reactions of the anions $CpM(CO)_3^-$ with Group IV organometallic halides of the formula R_3MX (R = Me, Et, n-Pr, Ph; M = Ge, Sn or Pb) readily afford $CpM(CO)_3MR_3$ products [189, 190]. Thermal stabilities of these complexes increase W > Mo > Cr. The first complex reported containing a Mo–Si bond is $CpMo(CO)_3SiCl_3$, isolated from the reaction of $[CpMo(CO)_3]_2$ and $HSiCl_3$ [191]. The corresponding trimethylsilyl derivatives of Mo and W were subsequently prepared by the reaction of $CpM(CO)_3H$ with $Me_3Si{-}NMe_2$ [192]. The best route currently available for synthesis of such complexes is the reaction of $Me_3M'{-}C_5H_5$ with $(CH_3CN)_3M(CO)_3$. This route is general for all the Group VI metals, but is restricted to $M' = Ge$ or Sn [193]. The corresponding reactions with the silicon derivatives leads to formation of dimeric products $[(Me_3SiC_5H_4)M(CO)_3]_2$ [194]. The reasons for this difference in behavior are uncertain. The "parent" compounds $CpM(CO)_3SiH_3$ have recently been synthesized from H_3SiBr and $K[CpM(CO)_3]$ [195]. The metal–metal bond is readily cleaved by water and HCl. The properties of these complexes are compared to those of corresponding methyl derivatives, $CpM(CO)_3CH_3$ [195].

Bonds between the $CpM(CO)_3$ moiety and copper or gold complexes have been generated by the reaction below [196].

$$Na[CpM(CO)_3] + ClM'L \rightarrow CpM(CO)_3M'L + NaCl$$

$(M = Cr, Mo, W;\ M' = Au, Cu;\ L = PR_3 \text{ or } AsR_3)$

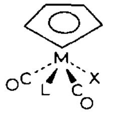
The complex $CpW(CO)_3Au(PPh_3)$ [197] has been shown to have the "piano-stool" geometry characteristic of these complexes, the W–Au bond being slightly shorter than the sum of the covalent radii.

This treatment has been brief, but the brevity is intentional. Reactions of the complexes discussed in this section have not been studied in detail and our purpose has been to give the reader an appreciation of the types of complexes currently known. For a review of the subject of heteronuclear metal–metal bonds we suggest consultation of references 180 and 198.

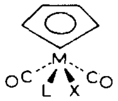
V. STEREOCHEMISTRY AND FLUXIONAL BEHAVIOR

A. Asymmetric transition metal atoms

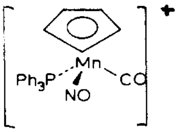
The possibility of the existence of isomerism in complexes of the general formula $CpMo(CO)_2(L)X$ was first pointed out by King in 1963 [102]. This isomerism results from the possibility of L being *cis* or *trans* to X in the distorted square pyramidal structure adopted by these complexes in the solid state, the C_5H_5 ligand occupying the apical position [25, 28, 31, 199].



cis



trans



In addition the *cis* form is potentially resolvable athough no examples where this has been accomplished are known at present. Isolable asymmetric complexes are known for Group VII metals where several examples of asymmetric manganese cyclopentadienyl complexes such as $[CpMn(CO)(NO)PPh_3]^+PF_6^-$ have been prepared by Brunner [200].

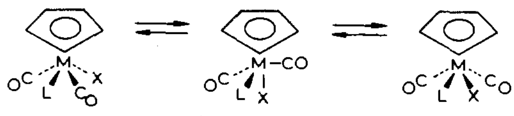
Neither are examples of asymmetric 1,2- or 1,3-disubstituted cyclopentadienyl Group VI metal complexes known. On the other hand, numerous examples of such complexes exist for Group VII and Group VIII transition metals[201].

The existence of both *cis* and *trans* isomers in solution for the molybdenum complexes in which L is a phosphine or phosphite and X is halide, hydride or alkyl has been unequivocally demonstrated by NMR techniques [126, 127]. These authors made elegant use of the fact that in the *cis* isomers the molybdenum atom is an asymmetric center. From straightforward symmetry considerations Faller and Anderson deduced that the methylene protons of *cis*-$CpMo(CO)_2(L)CH_2Ph$ would give rise to an ABX pattern where the methylene protons are nonequivalent and in addition are coupled to phosphorus [126]. (Somewhat similarly, an AB quartet is found for the methylene protons of a series of 2-substituted dimethylaminomethylferrocenes [202].) The *trans* isomer, having a plane of symmetry, should afford only a doublet methylene resonance, the multiplicity being due to phosphorus–hydrogen coupling. This in fact is what is observed. Furthermore, the multiplicities of the methylene resonances for *cis*- and *trans*-$CpMo(CO)_2(PPh_3)$ CH_2Ph were correlated with the observed singlet and doublet C_5H_5 resonances, respectively. The "singlet = *cis*, doublet = *trans*" criterion for assigning configuration to such isomers had been advanced previously [40, 101, 128]. Similar analysis of a series of CpW complexes has been reported [203].

Mawby and Wright made use of these same principles in assigning configurations to the series of complexes $CpMo(CO)_2(PMe_2Ph)X$ where X = Cl, Br, I[127]. In these compounds the methyl groups on phosphorus are magnetically equivalent in the *trans*- but not in the *cis*-isomer. The chloro and bromo complexes exhibit a singlet C_5H_5 resonance and two P–Me doublets. The iodo compound shows a corresponding singlet C_5H_5/double doublet PMe_2 pattern and a doublet C_5H_5/doublet PMe_2 pattern. Thus the chloro and bromo complexes exist as *cis*-isomers only but the iodo compound exists in solution as a mixture of *cis* and *trans* forms.

There has been considerable effort devoted to elucidating the nature of the interconversion and the reasons for the varying *cis*/*trans* ratios in the complexes $CpM(CO)_2(L)X$ as a function of L and X. The importance of steric effects is demonstrated by the decrease in *cis*/*trans* ratios with $Cl > Br > I$, $H > CH_3 > CH_2Ph$ (constant L) and $P(OMe)_3 > P(n\text{-}Bu)_3 > PPh_3$ (X = H) [126]. The latter results are in good agreement with the calculations of Tolman as to the steric demand of the phosphorus ligand [204]. The halide- and hydride-alkyl data obviously reflect the increasing size of X. Thus crowding would seem to favor formation of *trans*-isomers, as expected. Anomalous are encountered, particularly noteworthy being the apparent ability of $P(OPh)_3$ to stabilize the *trans*-isomer regardless of the nature of X. Also, surprisingly high proportions of *trans*-$CpMo(CO)_2(L)H$ are obtained considering the small steric demands of the hydride ligand [126]. From the electronic standpoint, certain of the isomerization data point to a possible "*trans* influence" in these complexes but further work is needed to support this view [126]. It seems reasonable to conclude, however, that a delicate balance of steric and electronic effects is at work in these systems and a simple explanation will probably not be forthcoming.

There is general agreement that the isomerization process, as observed by variable-temperature NMR spectroscopy, involves a pseudo trigonal bipyramidal transition state as depicted below [126, 205, 206]. Topological considerations have led to the conclusion that either L or X occupies an apical position in the intermediate/transition state:



Dissociative mechanisms as have been postulated for the disproportionation [207] and the racemization [208] of certain ferrocene derivatives have been excluded by observation that P–H coupling, ^{13}C–H coupling and ^{133}W–H coupling are retained in the high temperature averaged spectra [209, 210].

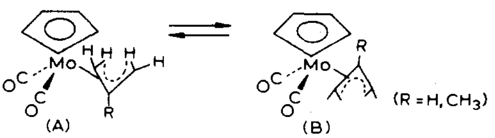
Similarly, *cis–trans* isomerism is to be expected for complexes of the formula $CpMo(CO)(L)_2X$. This has recently been demonstrated by a temperature-dependent proton NMR study of $CpMo(CO)(PMePh_2)_2Cl$ [211]. At 25° the spectrum is consistent with the presence of a single isomer exhibiting a singlet C_5H_5 resonance and coupling of both phosphorus atoms to the methyl protons. However, at −62° two distinct C_5H_5 resonances and a complex methyl pattern are observed. Further work in this area is to be expected, although such disubstituted complexes are difficultly accessible, as pointed out in Section IV.

Line shape analysis has also allowed Faller and Anderson to deduce a direct *cis-cis* interconversion (racemization) for the complex $CpMo(CO)_2(PMe_2Ph)I$ [126]. Nonequivalence of the diastereotopic methyl resonances of the *cis* isomer is almost completely averaged out before *cis–trans* isomerization occurs at appreciable rate. Similar results have been found for the π-indenyl complex π-$C_9H_7Mo(CO)_2(PMe_2Ph)I$ [205].

B. Fluxional behavior

Several cyclopentadienylmolybdenum and -tungsten complexes have been studied that were found to exhibit fluxional behavior ★. The simplest of these contains the $CpM(CO)_2$ group, the inert gas configuration being completed by complexation of a three-electron donor ligand of the π-allyl type.

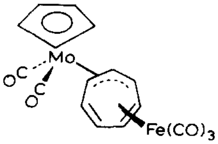
The complexes $CpMo(CO)_2$-π-C_3H_5 and $CpMo(CO)_2$-π-$C_3H_4CH_3$ exhibit four infrared carbonyl stretching bands rather than the two bands expected from symmetry considerations [213]. In addition, the PMR spectra of these compounds are temperature dependent. These features have been interpreted in terms of equilibria between the isomers shown below:



★ For an excellent review of the scope and definition of fluxional molecules see ref. 212.

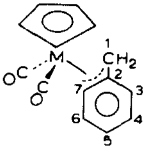
Barriers to interconversion are higher for the methallyl complex, apparently due to steric interaction of the CH_3 group with the C_5H_5 ring. An interesting method of differentiating the configuration of isomers A and B has recenlty been proposed [214]. Comparison of the chemical shifts of the central and anti protons of the allyl moiety in the cyclopentadienyl and corresponding indenyl Mo complex reveals a large anisotropic upfield shift for these protons in that indenyl isomer in which they are nearest the ring system. For example isomer A (R = H) is revealed as that having its central allyl proton pointed toward the aromatic ring by an observed $\Delta\delta$ of 3.46 ppm; similarly the anti protons in the other isomer possessed $\Delta\delta$ of 1.32 ppm thus allowing assignment of structure B [214].

The cycloheptatrienyl complex $CpMo(CO)_2(\pi\text{-}C_7H_7)$ exhibits a single resonance for the C_7H_7 protons at 25° but is "frozen out" at −113° to a mixture of isomers analogous to those for the allyl complexes cited above [215–218]. The room temperature averaged spectrum is accounted for by a series of rapid 1,2 shifts of the molybdenum atom about the C_7H_7 ring [218]. This same complex reacts with $Fe(CO)_5$ or $Fe_2(CO)_9$ to form a bimetallic complex in which $CpMo(CO)_2$ and $Fe(CO)_3$ are bonded to opposite faces of the C_7H_7 ring [219]:



At room temperature a sharp singlet is observed in the PMR spectrum for the C_7H_7 hydrogens. The temperature dependence of the spectrum has been explained by rapid movement of the Mo and Fe moieties around the opposite faces of the cycloheptatrienyl ring by 1,2 or a combination of 1,2 and 1,3 shifts [219].

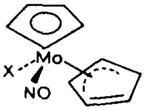
Thermal or photochemical decarbonylation of $CpM(CO)_3CH_2Ph$ [220] (M = Mo, W) complexes afford derivatives in which the benzyl (or substituted benzyl) ligand acts as a three-electron donor, two aromatic carbons being attached to the metal atom [220–222].



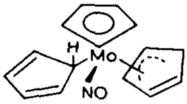
The PMR spectra of the complexes are deceptively simple at room temperature as a result of equilibration (NMR time scale) of the 3,4- and 4,6-protons. A study of the spectra as a function of temperature indicates a rearrangement process involving $CpM(CO)_2(\sigma\text{-benzyl})$. The tungsten compounds rearrange more slowly than their molybdenum counterparts, though the reasons for this are unclear at present [221].

Recently fluxional molybdenum complexes containing two or three C_5H_5 ligands have been reported. All of these cases differ significantly from the classic "ring whizzer"

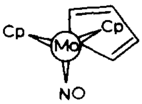
π-$C_5H_5Fe(CO)_2$-σ-C_5H_5 [223] in that differently bonded C_5H_5 groups interchange roles in their averaged spectra. The first such compounds reported were $Cp_2Mo(NO)I$ and $Cp_2Mo(NO)CH_3$ which showed a single C_5H_5 resonance at room temperature [224]. Counting electrons in the normal fashion would lead to the conclusion that these are 20 electron complexes, violating the inert gas 18 electron rule. King proposed that one of the C_5H_5's was distorted to participate in a π-allylic type interaction, and that rapid interchange of the Cp ligand roles could account for the average spectrum [224]. He has applied the term "interligand resonance" to this phenomenon [225].



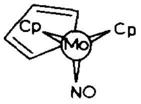
(X = I,CH$_3$)



More recent work in this area serves to contradict the above interpretation of this dynamic effect [226]. For Cp_3MoNO the room temperature PMR spectrum shows all 15 protons equivalent but as the temperature is lowered, a *monohapto*-Cp ring resonance first separates and then the other two rings begin to show separate singlet resonances. These observations are not inconsistent with a one h^1-, one h^3-, one h^5-Cp ring interpretation. However, the X-ray structure reveals that two Cp rings are essentially equivalently π-bonded to the metal but in skewed fashion [227]. The PMR differences observed between them below −80° is then attributable to hindered rotation about the Mo–C bond in the h^1-Cp ring such that the ring resides in one or the other of the two enantiomeric conformations shown in A and B:



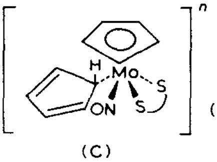
(A)



(B)

The two Cp rings reside in different magnetic environments. Latest results include a PMR study of $Cp_2Mo(NO)I$ and $Cp_2Mo(NO)CH_3$ down to temperatures approaching −120° [228]. Neither compound exhibits any broadening of the ten-proton singlet. In addition, a crystal study of the methyl complex reveals the same kind of skewed Cp ring arrangement as had earlier been found for Cp_3MoNO [229]. These observations would seem to argue against the interligand resonance interpretation.

Recently the complexes $Cp_2Mo(NO)(S_2CNMe_2)$ and $[Ph_4P]^+[Cp_2Mo(NO)S_2C_2(CN)_2]^-$



(n = 0, +1)

(C)

have been shown to undergo similar rearrangements [230]. These compounds apparently have structure (C) at 30° but the molecules become fluxional at higher temperatures, with the C_5H_5 ligands exchanging roles and giving rise to a single C_5H_5 resonance.

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