CHROMIUM, MOLYBDENUM AND TUNGSTEN

ANNUAL SURVEY COVERING THE YEAR 1975

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CONTENTS

Chromium, molybdenum and tungsten, Annual Survey covering the year 1974 see J. Organometal. Chem., 115(1976)221–325.

Abbreviations

acac - acetylacetonate
iso-butyl - Bu^i
n-butyl - Bu^n
tert-butyl - Bu^t
COT - 1,3,5-cyclooctatriene
Cp - cyclopentadienyl
DAB - glyoxalbis(*tert*-butyl)imine
diphos - 1,2-bis(diphenylphosphino)ethane
dipy - 2, 2'-dipyridyl
DMF - dimethylformamide
dmpe - 1,2-bis(dimethylphosphino)ethane
DPE - 1,2-bis(diphenylphosphino)ethylene
dpm - 1,2-bis(diphenylphosphino)methane
DTH - 2,5-dithiahexane
Et - ethyl
Me - methyl
NBD - norbornadiene
Ph - phenyl
o-phen, phen - *o*-phenanthroline
py - pyridine
R_f - perfluoroalkyl, -aryl
sal - salicylaldehyde
TCNE - tetracyanoethylene
THF - tetrahydrofuran
TNB - 1,3,5-trinitrobenzene

Introduction

This marks the first year of a collaboration in writing this section of *Annual Surveys* between Professors Donald J. Darensbourg and Marcetta Y. Darensbourg (Tulane University, New Orleans, Louisiana 70118, U. S. A.) and myself, during which I shall write the review for odd-numbered years, they for even-numbered years. The format developed over the past six years will be retained. The principle journals are covered directly for all the 1975 issues, and as a supplement, a computer search of Chemical Abstracts has been employed to obtain less-available references. The search was carried out late in 1976 to insure coverage of most 1975 references.

The reader's attention is again called to the fact that structural studies are reviewed in another section of Annual Surveys. These references thus will not be covered in detail, but will, rather, be covered alphabetically, by author, for the convenience of those reading this survey. Each year a number of reviews dealing wholly or in part with Group VI-B organometallic chemistry are published. These will be listed by title only, but these listings should provide a better estimate of the scope of interest in organometallic complexes of Cr, Mo and W from year to year.

The general format is, with minor exceptions, identical to last year's. Molecular nitrogen and nitrosyl complexes will be treated only insofar as they are true organometallic complexes, *i. e.*, contain a Group VI-B metal-carbon bond or are prepared from a species which does. Only those catalysis studies in which a reactant, product or catalyst is a true organometallic species or in which such a species is isolated as an intermediate will be reviewed. Abbreviations employed for conciseness are defined in the table above, and at the point in the manuscript where they are first employed.

The authors solicit suggestions for improvement in the usefulness of these surveys, and request reprints of relevant work, since human limitations will dictate the occasional inadvertent omission of papers in this area.

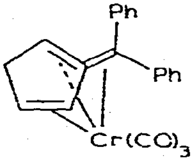
Dissertations

A number of dissertations have involved the synthesis and study of simple substitution products of the Group VI-B metal carbonyls. Bares has investigated diimine-Group VI-B metal carbonyls and their electrochemical reduction to afford singlet-state dianions.[1] The investigation of thiocarbonyl metal pentacarbonyls, $(SC)M(CO)_5$ (M = Cr, W), and their reactions with electrophiles *via* attack at sulfur was the subject of a dissertation by Dombek.[2] Simple substitution products of $Mo(CO)_6$ with $Ph_nP(CH_2CH_2CH{=}CH_2)_{3-n}$ (n = 1,2, Ph = phenyl) were studied by Garrou,[3] while Hohmann investigated highly-substituted, electron-rich derivatives containing phosphine ligands.[4] Derivatives of multidentate ligands have been prepared by Lemke,[5] who employed sulfur-containing macrocycles, and Mitchell,[6] whose dissertation explored the ^{31}P NMR spectra of derivatives containing bidentate organophosphine- and organophosphine sulfide ligands containing magnetically non-equivalent phosphoruses. Swanson prepared Group VI-B metal carbonyl azides, and studied their simple substitution reactions (with phosphines, for example), and their 1,3-cycloaddition reactions with trifluoroacetonitrile and hexafluoro-2-butyne.[7] Other synthetic studies have included preparation of $M(CO)_5X^-$ (X = F, OH, NO_3) derivatives and photochemical studies of the Group VI-B pentacarbonyls (Cihonski)[8], the preparation via metal atom synthesis, and NMR studies of bis(η-arene)Cr(0) complexes (Graves),[9] and the synthesis of $(\eta\text{-Cp})TlCr(CO)_3$ from $TlNO_3$ and $(\eta\text{-Cp})Cr(CO)_3^-$ (η-Cp = η-cyclopentadienyl) (Pedersen).[10] Burkhardt studied reactions of the phosphorus ylids with Group VI-B metal carbene complexes, and prepared diphenylcarbenepentacarbonyltungsten(0), and studied its reactions,[11] while Card[12] investigated reactions of η-arenetricarbonylchromium(0) complexes with alkyllithium reagents. Among other dissertations which involve cyclopentadienyl derivatives are included the synthesis of $(\eta\text{-Cp})(CO)W\text{-}\mu\text{-}C_5H_4Mn(CO)_4$ and isotopic labeling studies of its formation (Blickensderfer),[13] reactions of $(\eta\text{-Cp})M(CO)_3H$ (M = Mo, W) with Zn and Cd alkyls to afford symmetrical metal-metal bonded species, and determination of their structures (St. Denis)[14] and preparation of Tlm (m = $(\eta\text{-Cp})M(CO)_3$, M = Cr, Mo, W) (Theyson).[15] Hodges[16] has studied reactions of α-chloroenamines with transition metal carbonyl anions. Physical studies have included magnetic circular dichroism investigations of $M(CO)_6$ and $XM(CO)_5^-$ (M = Cr, Mo, W; X = Cl, Br, I) by Gall,[17] the determination of the crystal and molecular structure of trimethylenemethanetriphenylphosphinetricarbonylchromium(0) by Henslee,[18] dynamic ^{13}C NMR spectroscopy of (1,3,5,7-tetramethylcyclooctatetraene)$Cr(CO)_3$ and (cyclooctatetraene)$Cr(CO)_3$ by Hunter,[19] and a kinetic study of the reaction of $(\eta\text{-Cp})_2WH_2$ with benzotrichloride, and investigations of the reaction of sodium trichloroacetate with $M(CO)_6$ (M = Mo, W) and $(\eta\text{-}C_6H_6)_2Cr$, by Morrison.[20]

Pribula attempted the measurement of K_{eq} for (amine)$W(CO)_5$ equilibria,[21] and Wong investigated coordinatively-unsaturated Cp and C_9H_7 sandwich compounds of Cr, Mo, and W and their reactions with CO, olefins and acetylenes.[22] Catalysis has also been the subject of recent university research, by Woon, who studied the linear polymerization of terminal and internal acetylenes by (η-arene)$M(CO)_3$ complexes,[23] and by Photis, who investigated the $Mo(CO)_6$-promoted rearrangement of unsaturated propellanes, stable bond-shift isomers of cyclooctatetraenes.[24]

Structural Studies

A number of structural studies of Group VI-B organometallic complexes have been reported over the past year[25-68] (Fig. I-XVI).



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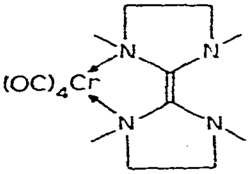

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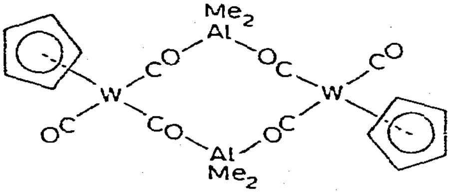

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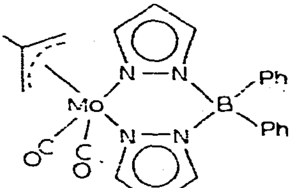

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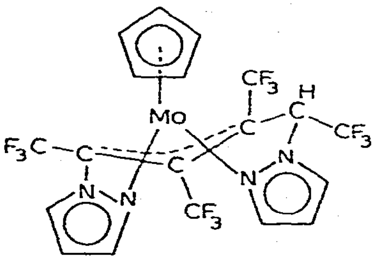

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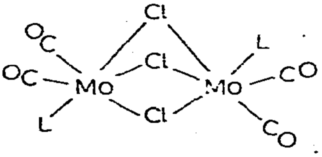

(L = P(OMe)3)

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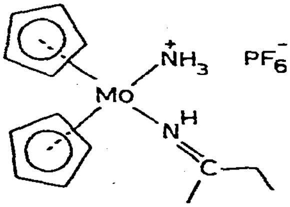

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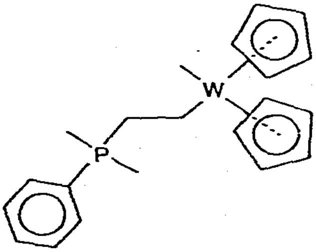

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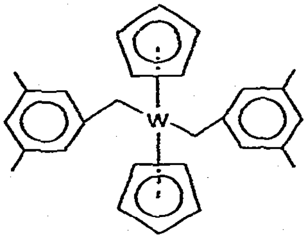

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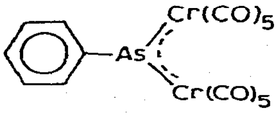

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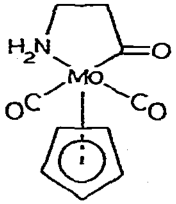

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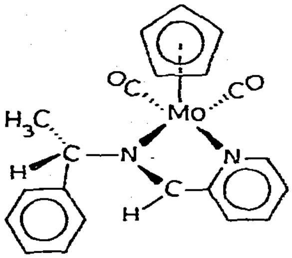

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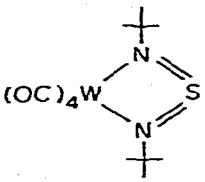

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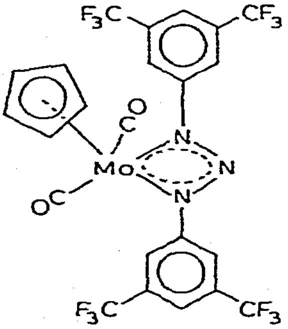
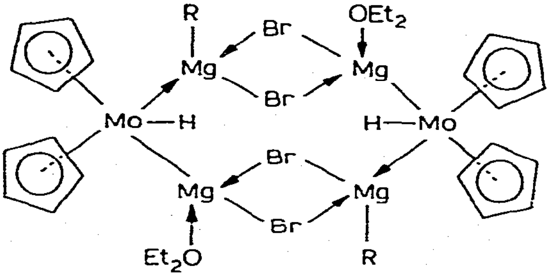


(XIV)

Reviews

Several reviews dealing wholly or in part with the organometallic chemistry of the Group VI-B metals were published in 1975.[69-85]



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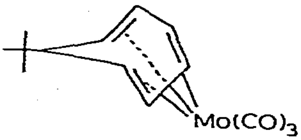
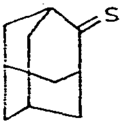


(XVI)

R = cyclohexyl, isopropyl (Pr^i)

Synthesis and Reactivity

Lewis base derivatives and related simple substitution products of metal carbonyls. A variety of simple substitution products of exotic and not-so-exotic Lewis bases and related compounds have been reported in the past year. Among the monodentate ligands which have replaced CO either thermally or photochemically to afford $LM(CO)_5$ complexes are adamantanethione (XVII), thiobenzophenone and ethylenetrithiocarbonate (XVIII),



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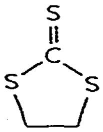

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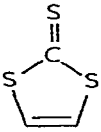
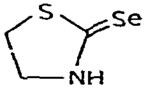


(XIX)

which afford dark purple derivatives bonded through the thione sulfur for all three metals (Cr, Mo, W),[86] 1,3-dithiolene-2-thione (XIX), also coordinated through the thione sulfur and prepared from $(NBD)M(CO)_4$ (M = Cr, Mo),[87] and thiazolidine-2-selenone (XX) and thiazolidine-2-one, in which each ligand is bonded through the *thioetheric* sulfur (M = Cr, Mo, W).[88] Monosubstituted derivatives of trithian (XXI) (R = H, Me) and of 1,3,5,7-tetrathiaoctane have also been synthesized, from $(THF)M(CO)_5$ (M = Cr, Mo, W; THF = tetrahydrofuran). For the trimethyltrithian complexes, temperature-dependent proton NMR spectra indicate a rapid intramolecular exchange among the possible S-bonding sites.[89] Simple pentacarbonyl complexes of thiazole (XXII), isothiazole (XXIII), 4-methylisothiazole and 5-methylisothiazole have been reported (M = Cr, W). Coordination is through N, and is similar to that in pyridine. Extensive mass spectral data are given and interpreted.[90] Darensbourg and Daigle have reported derivatives of phosphatriazaademantane (XXIV) and its N-analogue, urotropin.[91] Coordination in (XXIV) is through phosphorus, with analogous bonding in urotropin. The ligands can be alkylated with methyl iodide; the kinetics of the reaction of the P complex with $PhCH_2MgBr$ *via* attack at an equatorial carbonyl carbon to afford the a product containing the $M\text{-}C(R)=O^-$ functionality are very similar to those observed for reaction of $Me_3PCr(CO)_5$ with $PhCH_2MgBr$.[91] Carbonyl stretching spectra for a variety of mono- and disubstituted tungsten carbonyl-amine complexes,[92] and for $Mo(CO)_{6-n}L_n$ complexes for R_3P (R = *o*-, *m*-, *p*-ClC_6H_4, n = 0-3 (*trans* and *cis* for n = 2; *cis* for n = 3)) have been discussed.[93] Additionally, $M(CO)_{6-n}L_n$ derivatives of $P(C_2CMe_3)_3$ (= L; M = Cr, n = 1; M = Mo, W, n = 1,2) have been prepared through ultraviolet irradiation of the hexacarbonyl, or by displacement of polyolefinic ligands from the appropriate starting material. Infrared and ^{31}P NMR spectra have been discussed.[94]



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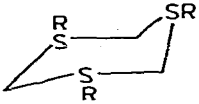

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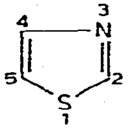

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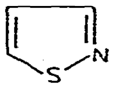


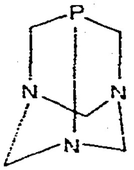
(XXIII)

Kraihanzel and Bartish have prepared (XXV, X = Cl) and have studied the inversion of configuration at P in this complex in methanol to afford (XXV, X = OMe). Proton NMR analysis indicates that the ring conformation in each isomer is probably chair, with $-Mo(CO)_5$ occupying an equatorial position. In the *trans*- -OMe complex, evidence supports an axial Bu^t substituent, and thus $-Mo(CO)_5$ has a greater site preference or holding ability than does Bu^t.[95]

Simple substitution products of tris(dimethylamino)stibine, prepared photochemically or thermally[96], and of $(Me_3)_3EBi$ (E =

C, Ge, Sn)[97] have also been described and infrared and proton NMR spectra for these complexes, and Raman spectra for the latter, have been presented and discussed. Malisch and Panster have prepared $(OC)_5MSbMe[M(CO)_3(\eta\text{-}Cp)]_2$ complexes through thermal or photochemical reaction of $M(CO)_6$ with $MeSb[M(CO)_3(\eta\text{-}Cp)]_2$. The complexes have been characterized by ^1H NMR, IR and mass spectral studies.[98]

Cornwell and Harrison have prepared simple substitution products (XXVI, R = R' = Me, CF_3; R = Me, R' = Ph or CF_3) of tin(II) bis(β-ketoenolates) under uv irradiation. Infrared, proton NMR and Mössbauer spectra support "synergic $\sigma+\pi$" bonding of tin to the transition metal.[99]



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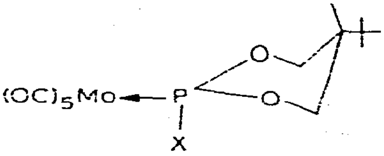

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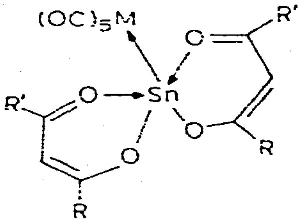


(XXVI)

Studies of monosubstituted Group VI-B metal carbonyls in which the ligand is the reactive site have also attracted attention. Sellmann and Thallmaier report the reaction of $Cr(CO)_5(NH_3)$ with acetone and cyclohexanone (OCR_2) to afford $(OC)_5Cr(NH{=}CR_2)$ products in the presence of base. The reactions probably proceed *via* formation of an $(OC)Cr(NH_2^-)$ intermediate.[100] Huttner and coworkers have treated $Cr(CO)_5(PPhH_2)$ and $(OC)_5Cr(AsPhH_2)$ with Bu^nLi (Bu^n = n-butyl) and have obtained $Cr(CO)_5(PPhHLi)$[101] and violet $(OC)_5Cr(AsPhLi_2)$[102] which, upon further reaction with N, N-dichlorocyclohexylamine affords the arsenidine complex whose structure is illustrated in (X).[102] Viewing the bonding in the Cr_2As moiety in terms of a 3-center 4π electron system affords a qualitative interpretation of the unusual electronic spectrum of (X).[51] Keiter and coworkers have studied reactions of $(OC)_5W(diphos)$ (=L) in which diphos functions as a monodentate ligand with Na_2PtCl_4 and $HgCl_2$ and have obtained the expected L_2PtCl_2 and $L_2Hg_2Cl_4$ (bridging chlorides) products; $(OC)_5W(Ph_2PC_2H_4P(O)Ph_2)$ was obtained as a by-product of the Pt reaction. Phosphorus-31 NMR spectra were discussed. Sellmann, Brandl and Endell have studied base-catalyzed H-D exchange in $N_2H_2[Cr(CO)_5]_2$. The observed H-D exchange, employing CD_3OD, is faster than exchange in the analogous NH_3 and N_2H_4 complexes, which was also studied. Disproportionation of $N_2H_2[Cr(CO)_5]_2$ (structure reported in reference 49) according to (1) was also investigated,

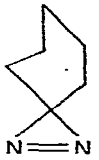
$$2\ N_2H_2[Cr(CO)_5]_2 \xrightarrow[\text{NaOMe}]{\text{THF/MeOH}} N_2H_4[Cr(CO)_5]_2 + 2\ Cr(CO)_5(THF) + N_2 \qquad (1)$$

A possible disproportionation mechanism, and the significance of (1) with respect to intermediate steps in nitrogen-fixation was discussed.[104] These workers have also studied the analogous Mo systems[105] and have prepared $N_2H_4[Mo(CO)_5]_2$ (hν, THF at low temperature) and from that complex, $(N_2H_4)_2[Mo(CO)_4]_2$, by similar methods. Prepared directly via use of uv irradiation in THF were $Mo(CO)_5(NH_3)$ and $Mo(CO)_5(N_2H_4)$. The latter complex could be oxidized to $(N_2H_2)[Mo(CO)_5]_2$ employing $H_2O_2/CuSO_4$, and all these complexes were deuterated (to the perdeutero analogues) employing KOD/THF ($Mo(CO)_5(NH_3)$), D_2O/THF ($Mo(CO)_5(N_2H_4)$ and $N_2H_4[Mo(CO)_5]_2$), and CD_3OD ($(N_2H_2)[Mo(CO)_5]_2$). The oxidation step may be related to initial steps in the fixation of molecular nitrogen. The Mo complexes exhibit the highest reactivity and lowest stability of all three Group VI-B metals in these systems.[105]

Potentially bidentate ligands which function as monodentate ligands have also been investigated by other workers. The dithiaalkanes $RSCH_2CH_2SR$ (=L, R = p-XC_6H_4, X = NO_2, Cl, H, Me, OMe, NMe_2) afford, depending upon the reaction conditions, complexes of the types $M(CO)_5L$, $[M(CO)_5]_2L$ and $M(CO)_4L$ (M = Cr, Mo). The complexes were characterized by IR, mass spectra, uv-visible spectra and proton NMR spectroscopy. Derivatives of the type $LM(CO)_5$ and $LM(CO)_4$ (M = Cr, Mo, W; L = ((cyclo-$C_6H_{11})_2PCH_2)_2$ have also been prepared.[107] Reaction of $LM(CO)_4$ with 1,2-bis-(dimethylphosphino)ethane (dmpe) afforded cis-L(dmpe)$M(CO)_2$; however, the corresponding $L_2M(CO)_2$ derivatives could not be obtained, probably as the result of unfavorable non-bonded interactions among the cyclohexyl groups in these species.[107] Study of ring-closure in $LM(CO)_5$ complexes was also carried out, and is discussed on page 440 .[106,107] Beck and Danzer have employed 1,2-diazaspiro[2.5]oct-1-ene (L, XXVII) to prepare $LW(CO)_5$ via displacement of acetonitrile from $(CH_3CN)W(CO)_5$.[108] The dimeric $L[W(CO)_5]_2$ could also be obtained in this way. Employing $(NBD)Mo(CO)_4$, $[LMo(CO)_4]_2$, in which two L bridge the two Mo atoms, was prepared. $(\eta\text{-CHT})Mo(CO)_3$ (CHT = 1,3,5-cycloheptatriene), and L gave $L_2Mo(CO)_3$ in which one L functions as a monodentate, and one as a bidentate ligand. The complexes were characterized through infrared and mass spectra.[108]

Monosubstituted derivatives have also been prepared employing $Na_2Cr_2(CO)_{10}$ as the substrate. Reaction of the dianion with nitrosobenzene or azoxybenzene affords azobenzene. However, reaction of 2-methyl-2-nitrosopropane with the dianion affords (t-butylamine)$Cr(CO)_5$.[109] Reaction of N, N-dichlorocyclohexylamine with $Na_2Cr_2(CO)_{10}$ yields $(C_6H_{11}N{=}NC_6H_{11})Cr(CO)_5$, in which the azocyclohexane ligand exhibits the trans configuration. The identity of the reaction product was confirmed by direct synthesis. Reaction of $C_6H_{11}NCl_2$ with $(OC)_5Cr(C(OLi)(n\text{-}C_4H_9))$ also gave the monosubstituted product; analogous reactions for M = Mo, W give poor yields.[110]

It is probable that the very large number of disubstituted derivatives reported stems in part from the stability and ease of isolation of (bidentate)$M(CO)_4$ complexes. Among tetracarbonyl derivatives containing chelating ligands which have been found to afford simple derivatives are (XXVIII), for M = Mo, W, which



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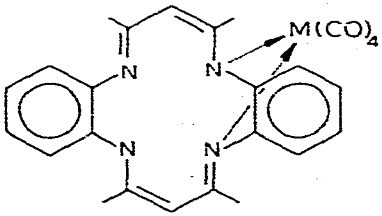
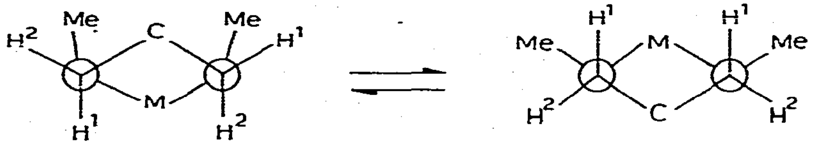


(XXVIII)

were prepared directly,[111] (XIII, ref. 57, M = Cr, Mo, W), prepared from $(CH_3CN)_3M(CO)_3$ and characterized by infrared and proton NMR,[112] $(Ph_2P(O)CH(Pr)PPh_2)M(CO)_4$, (M = Cr, Mo, W), also prepared directly and for which ^{31}P NMR spectral data were reported,[113] and $(Ph_2PCH_2NMeCH_2CH_2NMeCH_2PPh_2)Mo(CO)_4$, containing a nine-membered chelate ring, and which was obtained directly or from $(NBD)Mo(CO)_4$.[48]

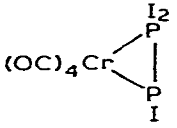
Hunter and Massey have prepared $((MeSeCH_2)_2CMe_2)M(CO)_4$ complexes (M = Cr, Mo, W) from $(MeSeCH_2)_2CMe_2$ and $(NBD)M(CO)_4$, and have studied their temperature-dependent NMR spectra, which are consistent with the intraconversion of two unequally populated, syn-configured symmetric chair conformers, (XXIX).



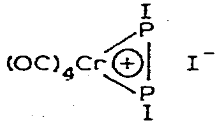
(XXIX)

Activation parameters for the process have been determined through line-shape analysis at differing temperatures.[114] Red-brown $(P_2I_3)Cr(CO)_4$, perhaps (XXX), has been obtained through reaction of P_2I_4 and $Na_2Cr(CO)_4$.[115] Its temperature-dependent ^{31}P NMR spectra indicate iodine-exchange between two phosphorus atoms. Exchange probably occurs through a symmetrical transition state such as (XXXI). Reaction of the complex with PPh_3 or $P(C_6H_{11})_3$ (L) affords red-brown complexes of stoichiometry $LCr(CO)_2PI_2$, probably dimeric.[115]

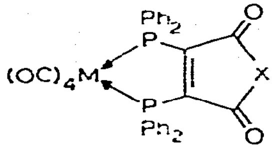
D. Fenske and Becher have studied solvatochromism in a variety of strongly colored complexes of 2,3-bis(diphenylphosphino)maleic anhydride derivatives (XXXII), (M = Cr, X = S; M = Mo, X = S, CH_2, NMe, PPh), in which the heteroatom of the maleic anhydride ring strongly influences the positions of low-energy absorption bands in the visible, attributable to n-π* transitions and is responsible for the observed solvatochromic effect.[116]



(XXX)



(XXXI)



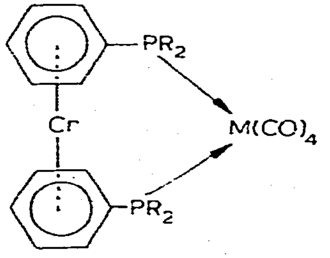
(XXXII)

Stelzer and Unger have studied reactions of coordinated ligands which have led to the formation of new complexes containing chelating ligands. Reaction of <u>cis</u>-$(PMe_2H)_2Mo(CO)_4$ with <u>n</u>-butyllithium to afford the corresponding PMe_2Li complex, followed by its reaction with a series of α,ω-dihaloalkanes afforded the series of complexes $[Me_2P(CH_2)_nPMe_2]Mo(CO)_4$ (n = 2-6), studied by infrared and ^1H and ^{31}P NMR. For n = 5 and 6, dimeric complexes in which the bidentate ligands function as bridges were also obtained.[117] Reaction of <u>cis</u>-$(PMe_2Li)_2Mo(CO)_4$ with $MeECl_2$ (E = P, As) led to the formation of tetracarbonylmolybdenum complexes containing the $Me_2PE(Me)E(Me)PMe_2$ ligand,[117,118] also characterized by NMR, infrared and mass spectra.

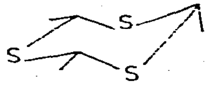
Reaction of $(\eta\text{-}C_6H_5PPh_2)_2Cr$ with $M(CO)_6$ (M = Cr, Mo, W) affords (XXXIII), which may be converted into green cation radicals through air-oxidation. ESR spectra for the latter indicate the unpaired electrons to reside in the $(\eta\text{-arene})_2Cr$ moiety.[119]

King and coworkers have investigated chelated derivatives of $Me_2PCH_2CH_2PPh_2$ prepared directly (M = Mo, W) and of $R'P(CH_2CH_2PR_2)_2$ (R' = Ph, R = Me; R' = Me, R = Me, Ph); the latter give facially trisubstituted complexes (M = Cr, Mo, W), prepared directly, or from $(CHT)M(CO)_3$. NMR spectra indicate that for the disubstituted derivatives which contain one chelating ring, there is a rapid ring inversion on the NMR time scale not observed in the trisubstituted complexes, which contain two such rings. The "triligate bimetallic complex," *cis*-$[MeP(C_2H_4PMe_2)_2]_2[Cr(CO)_4]_3$ was also obtained, from $(NBD)Cr(CO)_4$.[120]

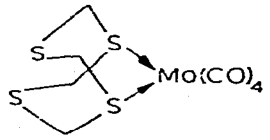
Schenk and Schmidt have prepared metal carbonyl derivatives of β-2,4,6-trimethyl-S-trithian (L; XXXIV) and 1,3,5,7-tetrathiacyclooctane (L'). The latter ligand reacts with $(NBD)Mo(CO)_4$ to afford (XXXV), while the Cr and Mo tricarbonyl derivatives of



(XXXIII)



(XXXIV)



(XXXV)

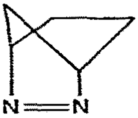
the first-named ligand, *facial*-$(CH_3CHS)_3M(CO)_3$ are synthesized from the appropriate tris(dioxane)metal tricarbonyl dimer. The tridentate ligand is readily displaced by Lewis bases such as $P(OPh)_3$. Mixed complexes, $(L)(dipy)[Mo(CO)_3]_2$ (dipy = 2,2'-dipyridyl), $[(HCHS)_3](dipy)[Mo(CO)_3]_2$ and $[(L')(dipy)Mo(CO)_3]_n$ (n = 1,2) in which L, L' and $(HCHS)_3$ function as monodentate or monodentate bridging ligands were also obtained, from $(CHT)Mo(CO)_3$, dipy, and the appropriate polythiaalkane.[121]

A number of other studies in which potentially bidentate ligands exhibit a variety of bonding types have also been reported. Clark and Stockwell have studied complexes of the ligands $CH_2{=}CHCH_2CH_2EMe_2$ (L; E = N, P, As) and observed that while L, E = N afforded only the "normal" chelated complexes,

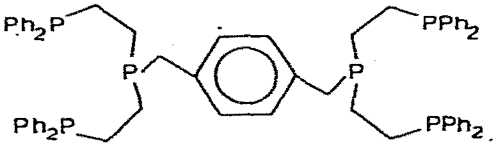
$LM(CO)_4$ (M = Cr, Mo, W), the P and As analogues afforded, in addition, mono- and disubstituted derivatives in which only E was coordinated to the metal. The IR, mass and NMR spectra for the complexes were taken, and the interconversion of rotational isomers in the chelated complexes was studied by variable temperature infrared spectroscopy.[122] The ligand 2,3-diazabicyclohept-2-ene (L; XXXVI) forms complexes of the types $L_2M(CO)_4$ (from $(NBD)M(CO)_4$), and $L_2[M(CO)_4]_2$ (two bridging ligands), and the analogous "mixed" species $L_2CrMo(CO)_8$.[123] Complexes of the types $LM(CO)_4$, *cis* and *trans*-$L_2M(CO)_2$ and *facial*-$L_2M(CO)_3$, in which one mono- and one bidentate ligand were coordinated and in which the monodentate L could be converted from the *cis* to *trans* form by ultraviolet irradiation, have been reported for *cis*-$Me_2As(CF_3)C{=}C(CF_3)AsMe_2$ (L; M = Cr, Mo and W).[124]

Among $L_2M(CO)_4$ complexes containing monodentate ligands, all prepared through use of standard synthetic techniques and characterized by typical methods, are *trans*-$L_2M(CO)_4$ (M = Cr, Mo, W; L = $(\text{cyclohexyl})_3P$ (no *cis* complexes or more highly-substituted derivatives could be obtained)[125], *cis* and *trans*-$L_2M(CO)_4$ (L = $(Me_3M')_3P$, M = Cr, Mo, W; M' = Sn, Ge)[126] and *cis*-$Mo(CO)_4L_2$ (L = $R_{3-n}P(NH_2)_n$; R = Me, Ph; n = 1, 2), prepared through reaction of the corresponding *cis*-$Mo(CO)_4(R_{3-n}PCl_n)_2$ complexes with $LiNH_2$ in liquid ammonia.[127] Phosphazenes of the type $RF_2P{=}N{-}PF_2$ (R = F, Ph) have also been employed in the synthesis of disubstituted derivatives, *cis*-$L_2Mo(CO)_4$, which are formed through displacement of NBD from $(NBD)Mo(CO)_4$. The phosphazenes were prepared through reaction of $[(Me_3Si)_2NPF_2]_2$ with RPF_4; $[(Me_3Si)_2NPF_2]_2$ also forms a *cis*-disubstituted complex.[128] Tetravinylsilane reacts with $M(CO)_6$ to form $[Cr(CO)_2]_2[Si(CH{=}CH_2)_4]_3$ and $[M(CO)_4]_2[Si(CH{=}CH_2)_4]$.[129]

Khan and Martell have found that the potentially tetradentate ligand (XXXVII) (= L) forms Cr and Mo complexes $[LM(CO)_3]_2$; IR and NMR spectra were employed in characterization.[130] The



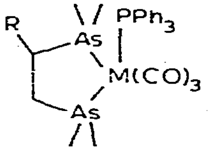
(XXXVI)

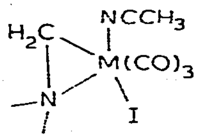


(XXXVII)

"mixed" derivatives (XXXVIII) have been synthesized through reaction of $[Me_2AsCH_2CH(R)AsMe_2]M(CO)_4$ (M = Mo, W; R = H, Bu^t)

with triphenylphosphine. Unlike the parent complexes (AS 1974/294), the mixed complexes contain the chelate ring locked in the chair configuration.[131] Reaction of tris(acetonitrile)-tricarbonylmetals (M = Mo, W) with dimethyl(methylene)ammonium iodide, $[Me_2\overset{+}{N}=CH_2][I^-]$, afforded the complexes (XXXIX). Reaction of these with diphos or dipy (E_2) affords the ionic species (XL).[132]


(XXXVIII)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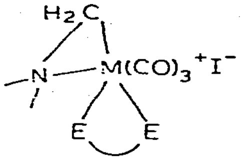
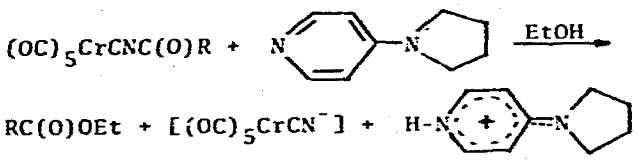
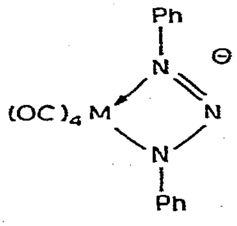

(XL)

Many other ionic simple substitution products have also been synthesized. Cihonski and Levenson have reported $M(CO)_5NO_3^-$ (M = Cr, W), synthesized through use of $M(CO)_5(THF)$,[133] and $W(CO)_5X^-$ (X = F, OH) and $Cr(CO)_5F^-$;[134] the hydroxide complexes were synthesized through use of [dibenzo-18 crown-6-K^+] cations; infrared, Raman and uv-visible spectra were obtained and discussed.[133-134] Kruck and coworkers prepared $Ph_4As^+[M(CO)_5SnF_3^-]$ (M = Cr, Mo, W) photochemically, and $Et_4N^+[Cr(CO)_5SnI_3^-]$ from $Cr(CO)_5(THF)$ and Et_4NSnI_3. The analogous Mo complex was also obtained, along with $Mo(CO)_5I$; the W complex was observed but not isolated. Insertion of SnX_2 into the M-Cl bond in $Et_4N^+[M(CO)_5Cl^-]$ (X = F, M = Cr; Mo, W; X = I; M = Cr) to afford $Et_4N^+[M(CO)_5SnClX_2^-]$ was also observed.[135] $Et_4N^+[R_3M'M(CO)_5^-]$ complexes (R_3M' = Ph_3Si, $MePh_2Si$, Ph_3Ge, Ph_3Sn, Me_3Sn, Ph_3Pb; M = Cr, Mo, W) have also been obtained through reaction of $R_3M'Li$ and $Et_4N^+[M(CO)_5Cl^-]$. For $[Ph_3SnW(CO)_5^-]$ and $[Cl_3SnW(CO)_5^-]$ these reactions lead to redistribution to the $[Ph_2ClSnW(CO)_5^-]$ and $[PhCl_2SnW(CO)_5^-]$ complexes. Reaction of $[Ph_3EW(CO)_5^-]$ anions with anhydrous HCl affords $[ClW(CO)_5^-]$ for E = Si or Ge, but $[Cl_3SnW(CO)_5^-]$ for E = Sn. Insertion of EX_2 into a W-X bond produces, e. g., the new complex $[Br_3SnW(CO)_5^-]$.[136] Pentacarbonylcarboxylate complexes, which employ $Bu^n{}_4N^+$ or Ph_4P^+ counter ions, $R_4E^+[M(CO)_5(OC(O)R')^-]$ (R' = Me, CF_3, M = Cr, Mo, W; R' = CCl_3, $C_{18}H_{35}$, M = Mo; R' = CMe_3, M = Cr, W and R' = H, M = W) have been synthesized from the appropriate pentacarbonyl halide salts and TlO_2CR', or directly. The carbonyl stretching spectra were interpreted in terms of less-than C_{4v} symmetry of the metal carbonyl fragment.[137] Höfle investigated reaction (2) and concluded the acylisocyanides react with nucleophiles in a manner similar to that observed for activated carboxylic acid derivatives.[138]

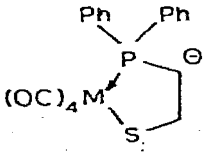


(2)

Behrens and Moll investigated the reactions of $Cr(CO)_5L$ (L = pyridine, $C_6H_{11}NC$) with $Na^+[(Me_3Si)_2N^-]$, which afforded the *cis*-$Na^+[Cr(CO)_4(L)(CN)^-]$ products, which were characterized by IR and NMR.[139] King and Nainan reacted sodium 1,3-diphenyltriazenide with the hexacarbonyls (M = Cr, Mo, W) and obtained (XLI).[140] Doyle allowed $TlPh_2PCH_2CH_2S$ to react with $M(CO)_5X^-$ to afford (XLII), isolated as the tetraethylammonium or tetraphenylarsonium salts (M = Cr, Mo, W).[141]



(XLI)

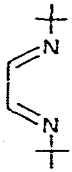


(XLII)

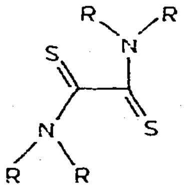
The previously reported $[(OC)_5WPPh_2(CH_2)_nPPh_2Me^+]I^-$ (n = 1,2) when heated afford the air-stable zwitterionic *cis*-$(OC)_4$-$(\overset{-}{I})W(PPh_2(CH_2)_n\overset{+}{P}Ph_2Me)$ species, characterized by uv-visible, IR and NMR spectra.[142]

Werner and coworkers have prepared yellow anionic *mer*-$Cr(CO)_3(M'Cl_3)_3^{3-}$ (M' = Ge, Sn), upon treatment of (borazene)-$Cr(CO)_3$ with $Ph_4As^+[M'Cl_3^-]$,[143] while Cullen and Pomeroy have obtained seven-coordinate, cationic $[(bidentate)M(CO)_4SnCl_3^+]$ ions, isolated as the $SnCl_5OH_2^-$ salts, upon treatment of $(bidentate)M(CO)_4$ (bidentate = diphos, $Me_2AsC_2H_4AsMe_2$, M = Mo, W) with $SnCl_4$.[144] (Also see Ref. 43). Finally, Ellis has obtained $M_2(CO)_{10}^{2-}$ over 20 hr through the Na/K reduction of the hexacarbonyls.[145]

Tom Dieck and coworkers have continued study of highly substituted (electron rich) Group VI-B metal carbonyl derivatives. Comparative studies of derivatives of glyoxalbis(*tert*-butyl)-imine (XLIII, DAB), and dipy (DAB and dipy = L) of the types $LM(CO)_4$, *cis*-$L(Bu^n{}_3P)Mo(CO)_3$ and *cis*-$L(Bu^n{}_3P)_2Mo(CO)_2$ and their paramagnetic monoanions (carbonyl stretching spectra, reduction potentials, ESR spectra of the monoanions (spin densities on the coordination sites) electronic spectra and observed solvatochromism, and ^{31}P NMR spectra) indicate that dipy is only about one-half as good a π-acceptor as DAB.[146] Complexes of analogous stoichiometries have been synthesized for ethanedithioamides, (XLIV, L; R = Me, Et; R$_2$ = -(CH$_2$)$_4$-, -(CH$_2$)$_5$-), LMo(CO)$_4$, LL'Mo(CO)$_3$ (L' = CH$_3$CN, PBu$^n{}_3$, PPh$_3$), and LL'$_2$Mo(CO)$_2$ (L' = PPh$_3$, PBu$^n{}_3$. Marked differences in the carbonyl stretching



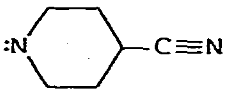
(XLIII)



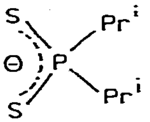
(XLIV)

frequencies for the tri- and tetrasubstituted complexes (much higher ν(CO) for the latter) suggest that in the trisubstituted derivatives the chelate ring is non-planar, while in the more "electron rich" tetrasubstituted species a coplanar "dithiolene type" ring system is present. Thus electronic factors induce a conformational change in these systems.[147] Acetonitrile has been replaced from (CH$_3$CN)$_2$L$_2$Mo(CO)$_2$ (L = PPh$_3$, PBu$^n{}_3$) and (CH$_3$CN)(PBu$^n{}_3$)$_3$Mo(CO)$_2$ by some twenty-six aromatic and α,β-unsaturated nitriles and dinitriles to afford yellow to red to blue products. For isonicotinonitrile (XLV) three complexes of the type (nitrile)$_2$(PPh$_3$)$_2$Mo(CO)$_2$ were observed, being the three possible complexes in which the two nitriles coordinate through either or both different ligand bonding sites, the nitrile, or the aliphatic nitrogen. Benzodinitrile affords polymeric products in analogous CH$_3$CN-replacement reactions. Acrylonitrile and other α,β-unsaturated nitriles form monosubstituted derivatives through replacement of acetonitrile from (CH$_3$CN)-(Bu$^n{}_3$P)$_3$Mo(CO)$_2$, and then further displace PBu$^n{}_3$ to become chelating ligands.[148]

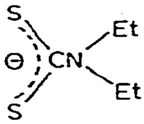
McDonald and coworkers have studied dithiophosphinate[149] and dithiocarbamate[150] (XLVI and XLVII, L) complexes, Mo(CO)$_2$L$_2$, the former prepared through reaction of Mo(CO)$_4$Cl$_2$ with HS$_2$PPr$^i{}_2$. For the dithiocarbamate complex, a non-linear Beer's law plot (visible spectrum) suggests the existence of a monomer-



(XLV)



(XLVI)

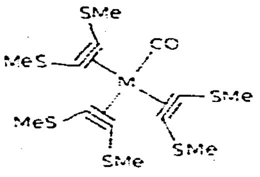


(XLVII)

dimer equilibrium.[150] Chemical behavior is similar in both systems.[149,150] The complexes reversibly add CO, and react with a variety of acetylenes to afford complexes of the type Mo(CO)-$(R_2C_2)L_2$ (HCCMe, HCCPh, Ph_2C_2, $(CH_3O_2)_2C_2$ and other substituted acetylenes); the acetylene is viewed as a four electron donor, affording the stable eighteen electron system. Acidification of solutions of the acetylene complexes affords some ethylene; thus these systems may be of possible interest as chemical models of nitrogenase activity in that that enzyme also reduces acetylenes to ethylenes.[149,150] For the dithiocarbamate substrate, forcing conditions also afford the 2:1 "adducts", $Mo(HCCPh)_2L_2$, and, additionally, $Mo(CO)_2L_2$ (L = dithiocarbamate) react with the diazene $EtO_2CN{=}NCO_2Et$ (L') to afford $Mo(L')(L)_2$ and $Mo(L')_2$-$(L)_2$ products, and with PPh_3 to afford $Mo(CO)_2(PPh_3)(L)_2$.[150]

Bond, Colton and Jackowski have studied the electrochemical oxidation of cis-$(dpm)_2M(CO)_2$ (dpm = 1,2-bis(diphenylphosphino)-methane; M = Cr, Mo, W). Cyclic voltammetry indicates that complexes of the types $(dpm)_2M(CO)_2{}^{0,+,++}$ exist; however, only the cis^0, trans$^+$ and cis^{++} species are thermodynamically stable. At low temperatures, however, the cis-trans isomerizations are slower, and vary in rate Cr<Mo<W. The results were compared to those for the analogous $(diphos)_2M(CO)_2$ complexes (AS 1974/215).[151] The chemical oxidations of cis-$(dpm)_2M(CO)_2$ and cis-$(diphos)_2M(CO)_2$ have also been compared.[152] Among oxidants which afford trans-$(dpm)_2M(CO)_2{}^+$ cations are Br_2, I_2, $NO^+PF_6{}^-$, $AgClO_4$ and HgX_2 (X = F, Cl, Br, I). Treatment of $(dpm)_2M(CO)_2$ with $O_2/HClO_4$ afforded diamagnetic, monomeric, seven-coordinate trans-$[M^{II}(dpm)_2(CO)_2H^+]$, believed to be capped octahedra. Infrared, ESR and NMR spectra were utilized in the characterization of these species. Reaction of cis-$(dpm)_2Mo(CO)_2$ with X_2 (X = Br, I) in CH_2Cl_2 afforded diamagnetic cis-$[(dpm)_2Mo(CO)_2X^+]$; for Br_2 the trans isomer was also observed.[152]

The acetylene MeSCCSMe has been found to react with $(CH_3CN)_3$-$M(CO)_3$ (M = Cr, Mo, W) forming the expected $(MeSCCSMe)_3(CO)M$ (XLVIII) complexes (M = Mo, W), which were well-characterized.[153] For Cr, the $Cr(CO)_2(MeSCCSMe)_2$ species was obtained, which undergoes [4+2] π-cycloaddition to afford (XLIX). Reaction of (MeSCCSMe)$_3$M(CO) with 1,2-bis(dimethylphosphino)ethane (L) afforded W(CO)(L)(MeSCCSMe)$_2$, which, for tungsten, further yielded a second complex, possibly (L), upon addition of excess L.[153]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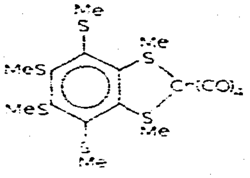
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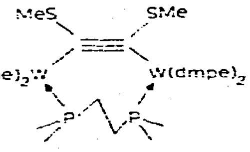

(L)

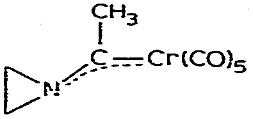
Mathieu and Poilblanc have studied the extent of replacement of P(OMe)$_3$ from M(CO)[P(OMe)$_3$]$_5$ complexes (M = Cr, Mo, W) by ligands (L) of varying steric and electronic properties.[154] For various L, the maximum extent of replacement was found to be (ligand, L, and number of P(OMe)$_3$ groups replaced for Cr, Mo, W given): NEt$_3$ (0,0,0); PMe$_2$Ph (1,1,0); PMePh$_2$ (0,0,0); PPh$_3$ (0,0,0); PMe$_3$ (2,1,0); P(OMe)Ph$_2$ (0,0,0); P(OMe)$_2$Ph (3,2,0); P(OCH$_2$)$_3$CEt (3,2,0). The results contrast to those of Tolman[155] for zerovalent Ni in that the degree of substitution is not exclusively a function of the steric demands imposed by L. Electronic factors, such as the strength of the M-P bond to be broken in the substitution process, are also of importance.

Dombek and Angelici have treated W(CO)(CS)[1,2-(diphenylphosphino)ethylene]$_2$ (= DPE) with alkylating agents [Et$_3$O$^+$]BF$_4^-$ and CH$_3$SO$_3$F to obtain the S-alkylation products (DPE)$_2$(CO)W(CSR)$^-$. In contrast, (DPE)$_2$W(CO)$_2$ reacted with [Et$_3$O$^+$]BF$_4^-$ to afford [EtW(CO)$_2$(DPE)$_2^+$][BF$_4^-$] in which the ethyl group is bonded to W. Reaction of the latter substrate with HCF$_3$SO$_3$ afforded [HW(CO)$_2$(DPE)$_2^+$][CF$_3$SO$_3^-$]; the thiocarbonyl is also protonated at the metal by CF$_3$SO$_3$H. Less highly substituted thiocarbonyls do not react with Et$_3$O$^+$, indicating the necessity of an electron-rich metal before S-alkylation can take place.[156] Trans-(OC)$_4$-W(CS)(I)$^-$ reacts with the electrophilic reagents acetic anhydride and trifluoracetic acid in the presence of BF$_3$ to afford the I(OC)$_4$W(CSCOCH$_3$) and -CSCOCF$_3$ complexes, and with alkylating agents to yield the corresponding -CSR complex. The results indicate the S of CS to be more nucleophilic than the O of CO.[156]

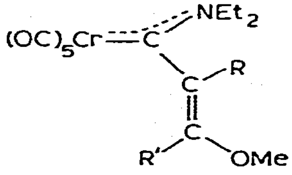
Edwards and Marshalsea report reactions of (CH$_3$CN)$_3$M(CO)$_3$ (M = Mo, W) with Cl$_2$ and Br$_2$ to afford MoCl$_4$(NCCH$_3$)$_2$, MoBr$_3$-(CH$_3$CN)$_3$ and WX$_4$(NCCH$_3$)$_3$, for which infrared spectra and magnetic moments are reported.[157] Ito and Yamamoto have studied reactions of $(diphos)_2Mo(C_2H_4)$ with a variety of reagents. With CF_3CO_2H, $Mo(O_2CCF_3)(diphos)_2^+$ and $Mo(O_2CCF_3)_2(diphos)_2$ are obtained, while with organic halides RX (R = Ph, X = Cl, Br, I; R = $PhCH_2$, X = Cl, and R = Me, X = I), $X_2Mo(diphos)_2$ species are obtained. The latter afford $H_4Mo(diphos)_2$ when allowed to react with $LiAlH_4$. Reaction of $(diphos)_2Mo(C_2H_4)$ with CO_2 under mild conditions affords a "CO_2 adduct." Under more rigorous conditions, <u>cis</u>-$Mo(CO)_2(diphos)_2$ is the observed product.[158]

Cotton, Kilner and coworkers have obtained L_4Mo_2, whose structure has been determined, and which contains a Mo-Mo quadruple bond, through reaction of $Mo(CO)_6$ and PhC(NPh)(NHPh) (L).[159,205]

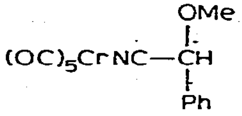
<u>Carbene and related complexes</u>. Studies of the formation and reaction of complexes containing carbene- and carbyne-like groups coordinated to the Group VI-B metals have attracted continued interest. King and von Stetten have prepared complexes (LI) through reaction of $(OC)_5Cr[C(OEt)(Me)]$ with ethyleneimine, and have tested their anti-cancer activity (no activity);[160] Dötz and Kreiter have studied reactions of $(OC)_5Cr[C(OMe)(R)]$ (R = Me, Ph) with $R'C{\equiv}CNEt_2$, (R' = H, Me) and have obtained (LII), which result from insertion of the alkyne entity into the metal-carbene bond. The products were characterized through IR and ^1H and ^{13}C NMR studies.[161] Fischer, Fontana and Schubert have reported results for the reaction of KCN with $(OC)_5Cr$-$[C(OMe)(Ph)]$ in methanol at room temperature, which afford the insertion-rearrangement product (LIII), as determined through standard analytical techniques.[162] The Fischer group has also investigated the complex reactions of transition metal carbene complexes with alcoholic alkoxides.[163,164] Depending upon the reaction conditions (relative qualities of OR^-) the anionic products given in 3-4 may be obtained. These may be alkylated



(LI)

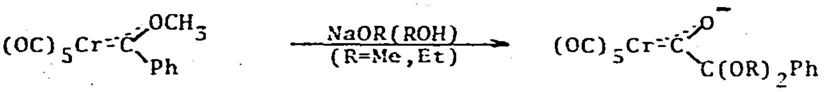


(LII)



(LIII)

with $R'_3O^+BF_4^-$ to afford the products (LIV) and (LV, M = Cr, W); (LIV, R = R' = Me) exchanges OCD_3 in D^4 methanol in the presence of catalytic quantities of $NaOCD_3$.[163]



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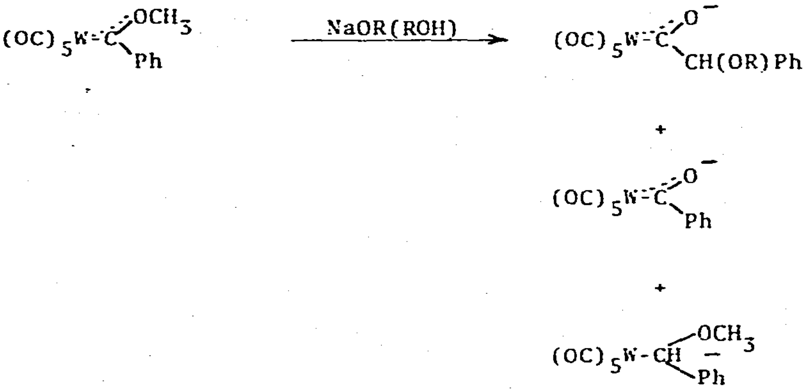
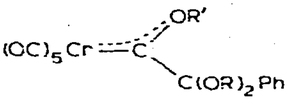
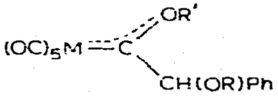


(4)

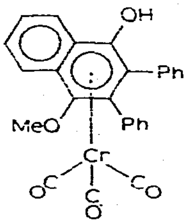
The employment of carbene complexes in organic synthesis has received further attention. Dötz has reported the synthesis of (LVI), which contains the napthol skeleton, through reaction of $(OC)_5Cr[C(OMe)(Ph)]$ with tolan (PhC≡CPh), as determined through IR and NMR studies, and the analysis of the degradation products of the complex.[165] Casey and Brunsvold have synthesized an exo-α-methylene-γ-butyrolactone (5-b) from methyl(methoxy)carbenepentacarbonylchromium, as is shown in scheme (5).[166]



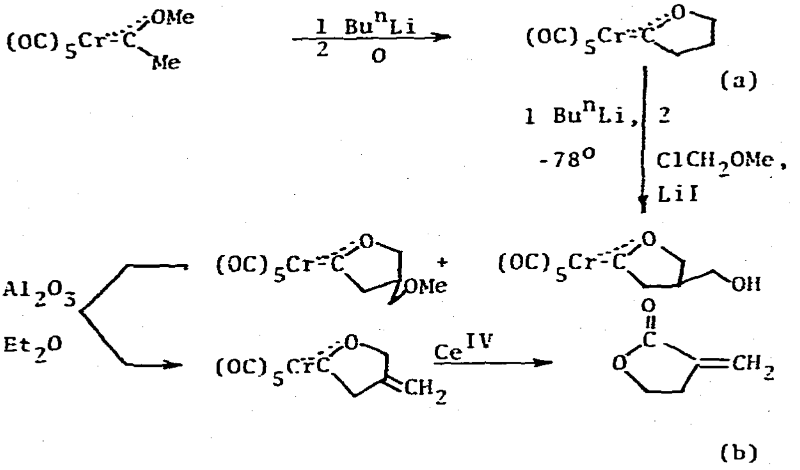
(LIV)



(LV)

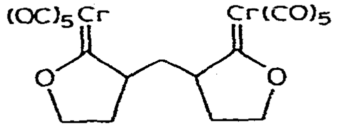


(LVI)



(5)

Treatment of (5-a) with one-half equivalent of $ClCH_2OCH_3$ affords (LVII).[166] Casey and Anderson have obtained evidence for a

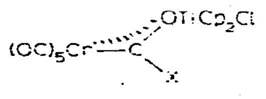


(LVII)

bimolecular mechanism for decomposition of (5-a), on the basis of analysis of kinetic and product data; the initial step is dissociation of a carbonyl, and evidence indicates that no free carbene is formed through the thermolysis.[167] The oxidation of $(OC)_5M[C(ER')(R)]$ complexes (M = W; R = Ph, ER' = OEt; R = Me, ER' = SPh; M = Cr; R = Me, ER' = $NHCH_2Ph$, SPh) employing pyridine-N-oxide, C_6H_5IO and ceric ammonium nitrate afford RCO(R') products, and thus offers a convenient method of characterization of transition metal carbenoid complexes.[168] Oxidation of $(\eta\text{-}Cp)Mo(CO)_2(PPh_3)(\overline{COCH_2CH_2CH_2})^+Br^-$ affords $\overline{C(O)OCH_2CH_2CH_2}$.[168] Treichel and Wagner have prepared yellow $(\eta\text{-}Cp)Mo(CO)_2(PPh_3)[C(OMe)(Me)]^+PF_6^-$ through reaction of $(\eta\text{-}Cp)Mo(CO)_2(PPh_3)[C(O)(Me)]^+$ with $MeOSO_2F$ followed by addition of ammonium hexafluorophosphate.[169] The product was characterized employing IR, NMR and conductivity data. Raubenheimer and Fischer have characterized the products (LVIII), obtained through reaction of $(OC)_5Cr[C(OLi)(X)]$ (X = Ph, NMe_2) with $(\eta\text{-}Cp)_2TiCl_2$, through use of IR, NMR and electronic spectral data. The product could not be alkylated employing triethyloxonium ion, presumably as a result of the covalent character of -C-O-Ti bonding.[170]

Fong and Wilkinson have prepared the carbene complex $Cr(CO)_5(CHNMe_2)$ through reaction of $[Cr(CO)_5{}^{=}]$ with $Me_2\overset{+}{N}{=}CH_2I^-$; the analogous reaction of piperidyl(methylene)ammonium chloride with $[Cr(CO)_5{}^{=}]$ affords $Cr(CO)_5[CHN(\underline{cyclo}\text{-}C_5H_{10})]$.[132]

The chemistry of compounds containing complexed carbyne ligands has also received attention this year. Reaction of $(OC)_5Cr[C(NEt_2)(OEt)]$ with boron tribromide in methylene chloride has been found by Fischer and coworkers to afford trans-$Br(OC)_4Cr(CNEt_2)$. Infrared, NMR and X-ray crystallographic analysis of this species have indicated a substantial contribution of (LIX-b) to a resonance description of bonding.[171]

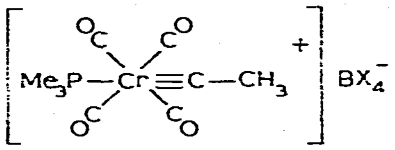


(LVIII)

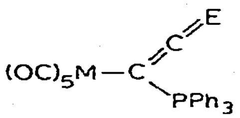
(LIX)

In contrast, trans-$(Me_3P)(OC)_4Cr[C(OMe)(Me)]$ reacts with BX_3 (X = Cl, Br) at low temperature in pentane to afford (LX); it is proposed that that cationic species arises when the position trans to the carbyne ligand is blocked, preventing an anionic X^- from entering.[172] The trans-$Br(OC)_4Cr(CR)$ complexes (R = Me, Ph) react with dicobalt octacarbonyl to afford $(RC)Co_3(CO)_9$; this reaction is the first reported transfer of a carbyne ligand from metal to metal.[173] Reaction of $(OC)_4Cr(C\text{-}\underline{p}\text{-tolyl})$ with trimethylphosphine in methylene chloride at -50° affords a wine-red product (LXI), characterized through NMR spectroscopy.[174] Kreissl and Held have also prepared the ylid complex $(OC)_5W(CPh_2PMe_3)$ through the low temperature reaction of $(OC)_5W(CPh_2)$ with trimethylphosphine.[175]

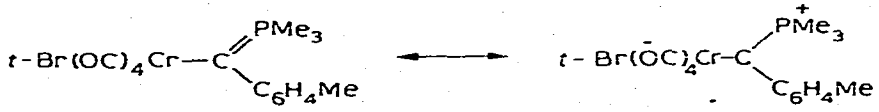
Lindner has reviewed recent advances in metal carbonyl ylid chemistry which have been made in his laboratory.[176] Reaction of (acetonitrile)pentacarbonylmetal(0) complexes (M = Cr, W) or molybdenum hexacarbonyl with $E{=}C{=}\ddot{C}{=}PPh_3$ (E = O, S) affords the yellow products (LXII) characterized by infrared and mass spectrometry. These ligands possess little π-accepting ability, and are readily exchanged by weakly basic solvents such as THF and DMF (dimethylformamide). The $(OC)_5M[C(PPh_3)(CO)]$ complexes extrude carbonylmethylene, :C=C=O, upon heating to afford $(OC)_5MPPh_3$ products. The carbonylmethylene can be



(LX)



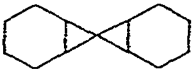
(LXII)



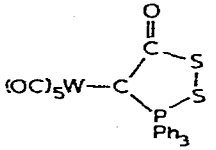
(LXI)

"trapped" through addition of cyclohexene; 7,7-spironorcarane (LXIII) is the observed product. The reaction of $(OC)_5W[C(PPh_3)(CO)]$ with S_6 at 110°affords (LXIV). Reaction of $(CH_3CN)Cr(CO)_5$ with the $:C(SPh)_2(PPh_3)$ "ylid" affords the simple substitution product, which reacts with S_6 at 20° by a Wittig-like process to afford the orange-red carbene, $(OC)_5Cr[C(SPh)_2]$.[176]

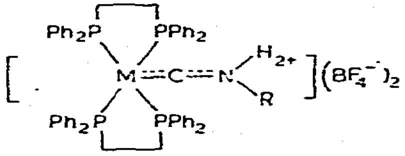
Chatt and coworkers have studied reactions of trans-$M(N_2)_2(diphos)_2$ with isonitriles. They afford trans-$M(CNR)_2(diphos)_2$ products (M = Mo, W; R = Me, Bu^t, aryl). For M = Mo, R = Me, the structure has been determined through X-ray analysis.[30] Protonation of these complexes afford pink (LXV) products containing a carbyne-like ligand. Protonation or alkylation can also take place at nitrogen to afford complexes such as $[W\{CN(H)Me\}(CNMe)(diphos)_2{}^+]BF_4{}^-$ and $[M(CNMe_2)(CNMe)(diphos)_2{}^+]SO_3F^-$ (M = Mo, W), which are unstable in solution.[30]



(LXIII)



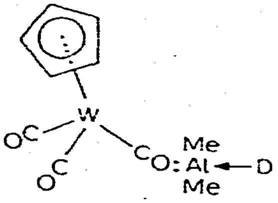
(LXIV)



(LXV)

η-Cyclopentadienyl, η-arene and other π-complexes. There has been great interest once again in the synthesis of "$(\eta\text{-}Cp)M(CO)_3X$" systems. Save for the most electropositive metals (Mg, Al), the $(\eta\text{-}Cp)M(CO)_3$ group is bonded to a formally one-electron donating substituent, which results in metal-metal bond formation. For the electropositive metals, the metals are joined by M:CO:M' bridges.

The reduction of $[(\eta\text{-Cp})Mo(CO)_3]_2$ or $(\eta\text{-Cp})Mo(CO)_3I$ with Mg/Hg in THF or benzene/pyridine (THF or pyridine = solv) results in the formation of $solv_4Mg[Mo(CO)_3]_2$, in which there is evidence for Mg-OC-Mo bridging and in which this bridge occupies an axial position with respect to the six-coordinate Mg atom. Monosubstituted substrates, $(\eta\text{-Cp})Mo(CO)_2(L)(I)$ (L = $PBu^n{}_3$, $PMePh_2$) afford analogous dicarbonyl species for which there is evidence for solv dissociation in solution.[177] The crystal structure for $[(\eta\text{-Cp})W(CO)_3(AlMe_2)]_2$, prepared from trimethylaluminum or dimethylaluminum hydride and $(\eta\text{-Cp})W(CO)_3H$ has been reported (Fig. III).[33] Cleavage of the twelve-membered W-CO-Al rings can be effected by HX (X = Cl, OH, acac) to afford the $(\eta\text{-Cp})W(CO)_3H$ starting materials, and by Lewis bases (D, = NMe_3, OEt_2) to afford (LXVI) species. The analogous $[(\eta\text{-Cp})W(CO)_2(L)(AlMe_2)]_2$ species were also prepared via $(\eta\text{-Cp})W(CO)_2(L)H$ (L = PMe_2Ph, PEt_2Ph, PPh_3). For the first two L, the phosphines replace the terminal CO's in structure (LXVI); the structure of the PPh_3-containing complex is uncertain.[33]



(LXVI)

The analogous reaction of $(\eta\text{-Cp})W(CO)_2(L)H$ (L = CO, PPh_3) with trimethylgallium affords $(\eta\text{-Cp})W(CO)_2(L)(GaMe_2)$ complexes. Upon heating, the tricarbonyl complex forms $[(\eta\text{-Cp})W(CO)_3]_2GaMe$ and $[(\eta\text{-Cp})W(CO)_3]_3Ga$. Unlike the Al complexes cited above,[33] the latter complex has been shown by X-ray crystallography to posess Ga-W bonds, rather than W-CO-Ga bridges.[34]

Pederson and Robinson have reported preparation of $Tl[(\eta\text{-Cp})Cr(CO)_3]$ (AS 1974/84) through reaction of $Na[(\eta\text{-Cp})Cr(CO)_3]$ and $TlNO_3$ in THF/water. This complex disproportionates to afford $Tl[(\eta\text{-Cp})Cr(CO)_3]_3$ upon standing; the analogous reaction for Mo forms only the Tl(III) complex.[178]

New silyl-vinyl complexes, $(\eta\text{-Cp})M(CO)_3(SiR_2CH{=}CH_2)$ (M = Mo, W; R = Me, Cl) have been synthesized by Malisch and Panster, and have been thoroughly characterized by IR, NMR, and MS. They were prepared through reaction of $Na[(\eta\text{-Cp})M(CO)_3]$ and $H_2C=$

$CHSiR_2Cl$. The Cl complexes can be converted to their F analogues through their reaction with $AgBF_4$. All can be decomposed in the presence of HX to afford $(\eta\text{-}Cp)M(CO)_3H$ and $XSiR_3$.[179]

Several types of complexes containing heavier Group VI-A metals have also been prepared. Reaction of $(\eta\text{-}Cp)Mo(CO)_3R$ (R = H, Me) with $[(Me_3Si)_2CH]_2Sn$ has been reported to afford $(\eta\text{-}Cp)Mo(CO)_3[Sn(R)(CH(SiMe_2)_2)]$,[36] and reaction of $[(\eta\text{-}Cp)Mo(CO)_3]_2$ with $(Me_3SiCH_2Sn)_2Hg$ affords $(\eta\text{-}Cp)Mo(CO)_3[Sn(CH_2SiMe_3)_3]$.[180] The reduction of $[(\eta\text{-}Cp)M(CO)_3]_2$ (M = Cr, Mo, W) with Na/K in THF has been found to afford the $(\eta\text{-}Cp)M(CO)_3^-$ anion cleanly, and in high yield. The synthetic utility of this preparation has been confirmed through synthesis of the known $(\eta\text{-}Cp)M(CO)_3$-Ph_3Sn complexes in 98-99 per cent yield.[181]

Cyclopentadienyltricarbonylmetal complexes containing M-Sb bonds have also been reported by Malisch and Panster. Thus $(\eta\text{-}Cp)M(CO)_3SbMe_2$ and $[(\eta\text{-}Cp)M(CO)_3]_2SbMe$ have been synthesized from $Na[(\eta\text{-}Cp)M(CO)_3]$ and Me_2SbBr (M = Cr, Mo, W)[182] and $MeSbBr_2$ (M = Mo, W)[183] respectively. The Sb in these species can be quaternized employing a variety of RX species (R = Me, Et, $PhCH_2$, $CH_2{=}CHCH_2$; X = Br, I) to afford the corresponding $(\eta\text{-}Cp)M(CO)_3$-$SbMe_2R^+$ and $[(\eta\text{-}Cp)M(CO)_3]_2SbMeR^+$ cations.[182,183] The $(\eta\text{-}Cp)M$-$(CO)_3SbMe_2$ complexes can be cleaved by phosphorus ylides, $Me_3\overset{+}{P}$-$\overset{-}{C}HR$, to afford the $(\eta\text{-}Cp)M(CO)_3^-$ anions (M = Mo, W) and $Me_3\overset{+}{P}$-CH_2-$SbMe_2$.[182] The $[(\eta\text{-}Cp)M(CO)_3]_2SbMeR^+$ cations can also be synthesized through reaction of $(\eta\text{-}Cp)M(CO)_3(SbMe_2)$ with $(\eta\text{-}Cp)M(CO)_3$-Br.[183] The $[(\eta\text{-}Cp)W(CO)_3]_2SbMe$ dimer also reacts with bromine to afford $[(\eta\text{-}Cp)W(CO)_3]_2(SbMeBr_2)$, in which Sb is pentacoordinate.[183] The complexes were characterized through proton NMR, mass and IR spectra.

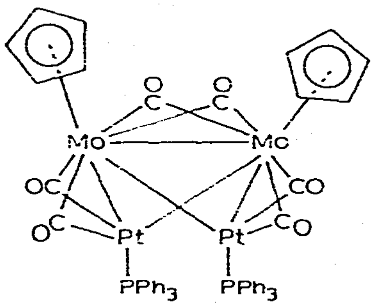
These workers have also studied reactions of $SbBr_3$ with the $(\eta\text{-}Cp)M(CO)_3^-$ anions.[184] These reactions afford $(\eta\text{-}Cp)(OC)_3$-$M\text{-}SbBr_2$ (M = Mo, W), which can react further with $(\eta\text{-}Cp)M'(CO)_3^-$ (M' = Mo, W, n = 3; M' = Fe, n = 2) to afford $(\eta\text{-}Cp)(OC)_3M$-Sb-(Br)-$M'(CO)_3(\eta\text{-}Cp)$, or with $M(CO)_5(THF)$ (M = Cr, Mo, W) to produce $(\eta\text{-}Cp)(OC)_3M(Br)_2Sb\text{-}M(CO)_5$. Treatment of $(\eta\text{-}Cp)(OC)_3MSbBr_2$ with bromine results in M-Sb bond-cleavage with formation of $(\eta\text{-}Cp)M(CO)_3Br$ or $(\eta\text{-}Cp)M(CO)_2Br_3$, presumably through formation of an intermediate containing five-coordinate Sb.[184]

Dehand and coworkers have synthesized cyclopentadienyltricarbonyl metal complexes containing Mo-Pt and Mo-Pd bonds.[185-186] The reaction of _trans_-PtL_2Cl_2 or _trans_-PdL_2Cl_2 (L = pyridine, 3-Mepy) with $(\eta\text{-}Cp)Mo(CO)_3^-$ in THF afforded the complexes _trans_-

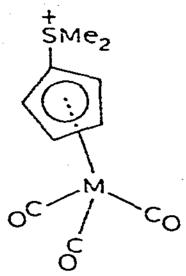
ML$_2$[Mo(CO)$_3$(η-Cp)]$_2$ (M = Pt, Pd), which were shown through a very extensive infrared study to contain linear M-Mo-M bonding; the (η-Cp)Mo(CO)$_3$ groups are strongly anionic in these complexes.[185] Reaction of the (η-Cp)Mo(CO)$_3^-$ anion with Et$_4$N$^+$AuCl$_2^-$ in THF also affords a complex containing a linear Mo-Au-Mo linkage, Et$_4$N-[(η-Cp)Mo(CO)$_3$]$_2$Au.[186] Reaction of (η-Cp)Mo(CO)$_3^-$ with cis-PtCl$_2$(PPh$_3$)$_2$ afforded two complexes, one containing Mo-Pt linkages and formulated as (LXVII), and the homotrimetallic Pt cluster complex, Pt$_3$(CO)$_2$(PPh$_3$)$_4$, in which the Pt$_3$(CO)$_2$ framework is analogous to that in triiron dodecarbonyl.[187]

Hackett and Manning have reported the preparation and reactions of new complexes containing Cu and Ag bonded to various transition metals, including Cr, Mo, W. The transformations are summarized in Eq. 6.[188] The complexes were characterized by IR and conductivity measurements.

Setkina and coworkers have prepared (LXVIII) through reaction of M(CO)$_6$ with dimethylsulfonium cyclopentadienylide in acetonitrile; the Mo complex was identified only through its

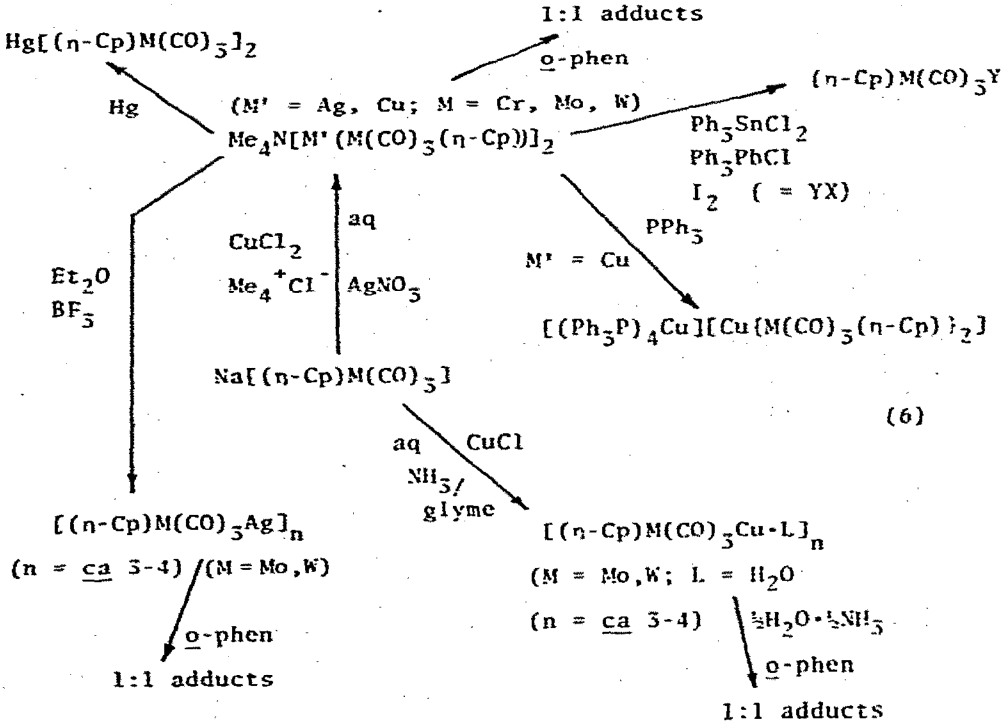


(LXVII)



(LXVIII)

spectral properties.[189] Other studies have emphasized the versatility of η-cyclopentadienyltricarbonyl species in their reactivity. Green and Hughes have studied reaction of (η-Cp)M(CO)$_3^-$ (M = Mo, W) with the 1,2-3-tri(t-butyl)cyclopropenium cation which affords (LXIX). Reaction of (LXIX) with CHCl$_3$ leads to replacement of H by Cl. This reaction represents an example of electrophilic substitution at the (η-Cp) ring.[190]

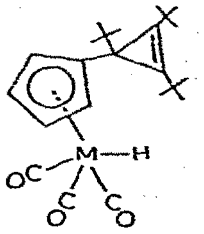


(6)

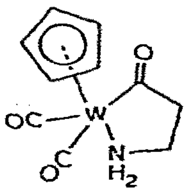
Reactions of $[(\eta\text{-Cp})M(CO)_3(\pi\text{-ethylene})^+]$ with nucleophiles coordinating through N, P, or O, and the cyanide ion (L) afford β-substituted ethylmetal derivatives, e. g., $[(\eta\text{-Cp})M(CO)_3CH_2CH_2L^+]$. The initial products tend to be dialkylated, as is illustrated in (7). Deprotonation of the cationic β-substituted

$$2[(\eta\text{-Cp})M(CO)_3C_2H_4^+] + NH_3 \rightarrow [(\eta\text{-Cp})M(CO)_3CH_2CH_2]_2NH_2^+ \qquad (7)$$

products with OH^- insertion affords insertion-cyclization products such as (LXX). A very wide variety of reaction products



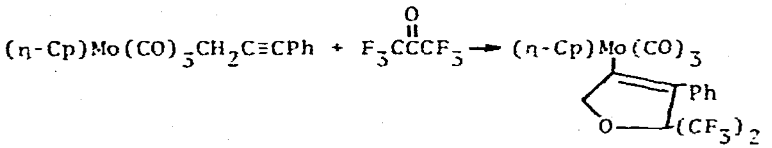
(LXIX)



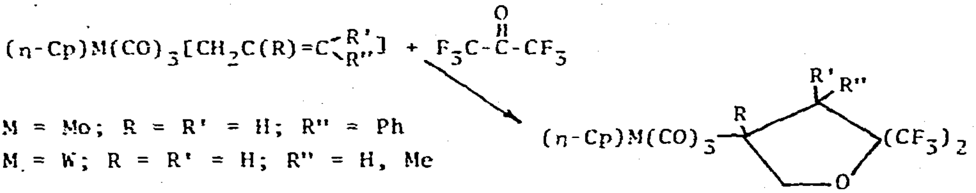
(LXX)

obtained for L such as NH_3, $MeNH_2$, PPh_3, py, Me_3N, etc. are reported.[191]

Lichtenberg and Wojcicki have studied [3 + 2] cycloaddition products of the reactions of metal-2-alkenyl and metal-2-alkynyl complexes with the electrophile hexafluoroacetone. The reactions are summarized in (8-9). The higher carbonyl stretching frequencies observed in the products are indicative of the strongly electron-withdrawing character of the organic ring systems.[192]



(8)



M = Mo; R = R' = H; R" = Ph
M = W; R = R' = H; R" = H, Me

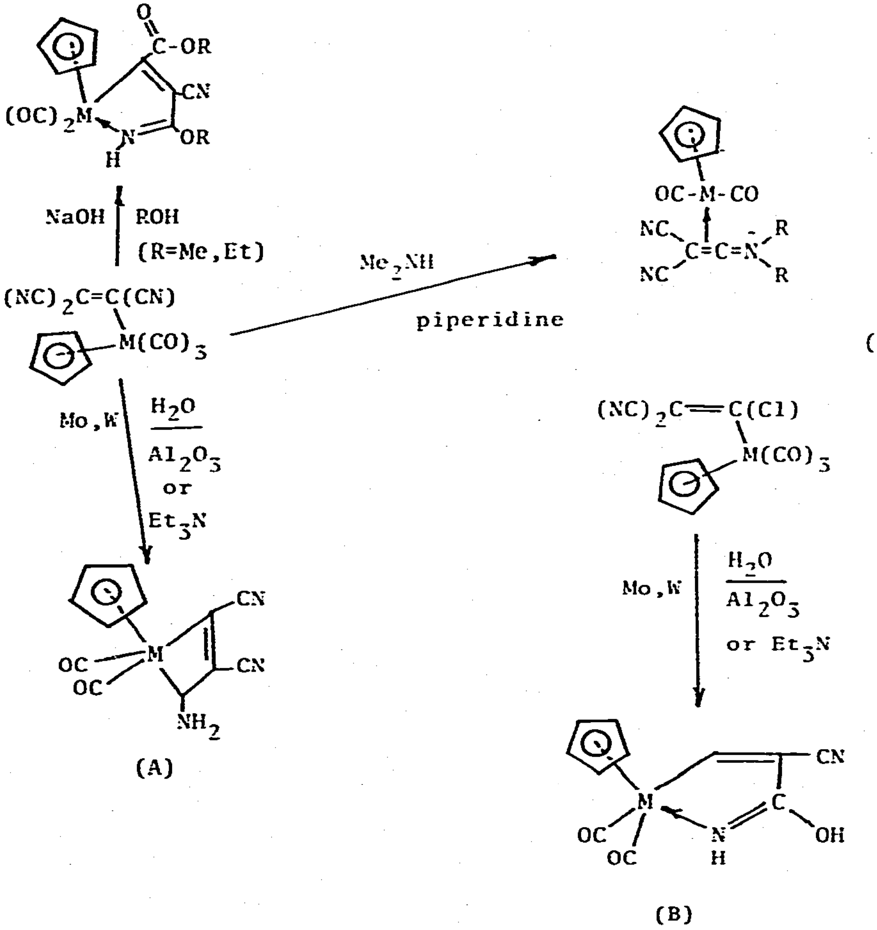
(9)

Wojcicki's group has also studied the electrophilic behavior of tetracyanoethylene (TCNE) toward transition metal-carbon σ-bonds.[193] Reactions of (η-Cp)$Mo(CO)_3R$ (R = Me, CH_2Ph) and (η-Cp)$Mo(CO)_2$(L)(Me) (L = PPh_3 $P(OPh)_3$) afford two types of "adducts", the first type arising from "normal" insertion of TCNE into the metal-R bond, $-C(CN)_2C(CN)_2CH_3$, the second containing the isomeric keteneiminato function, -N=C=C(CN)C(CN)R. In the dicarbonyl complexes, the four groups other than (η-Cp) usually adopt a trans configuration; however, IR evidence indicates that for $P(OPh)_3$ and -N=C=(CN)C(CN)R, which exert relatively unimportant steric demands, a cis configuration is observed. The structure of the "normal" insertion product for L = PPh_3, R = Me has been determined through X-ray analysis.[32]

Severson and Wojcicki have also noted that BF_3 increases the rate of SO_2 insertion into the W-C(R) bonds in (η-Cp)$W(CO)_3R$ (R = Me, CH_2Ph). The observed products are the (η-Cp)$W(CO)_3SO_2R$ complexes. The catalytic effect probably arises through an increase in the electrophilic strength of SO_2 upon complexation with BF_3.[194]

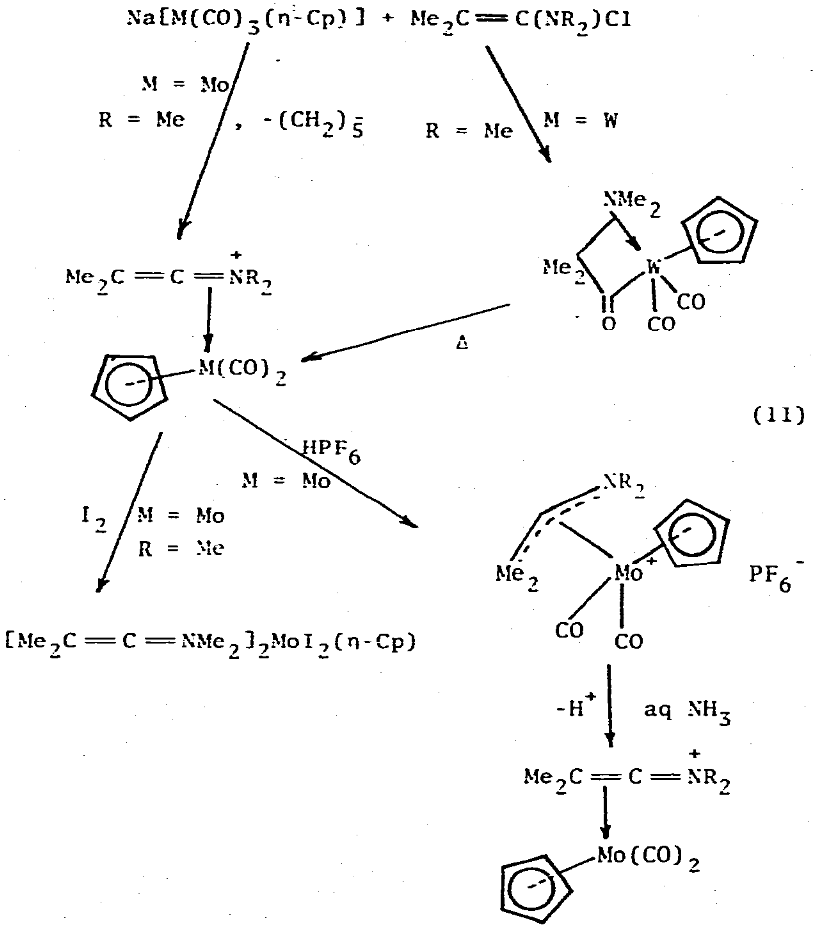
King and coworkers have reported the results of investigations of Group VI-B metal carbonyl anions with α-chloroenamines,[195] and the hydrolysis, aminolysis and alcoholysis of 1-chloro-2,2-

dicyanovinyl and tricyanovinyl derivatives of Mo and W.[196] The interconversions are summarized in (10) and (11), respectively. In the former study, product structures could be determined unequivocally through ^{13}C, and ^{1}H NMR and through observation of whether or not a ν(CO), acyl was observed in the IR spectrum.[195] In the latter investigation, possible mechanisms of complex interconversion were discussed.[196] Reactions of η-Cp and η-allyl molybdenum derivatives with alkyl isocyanides have also been discussed.[197]



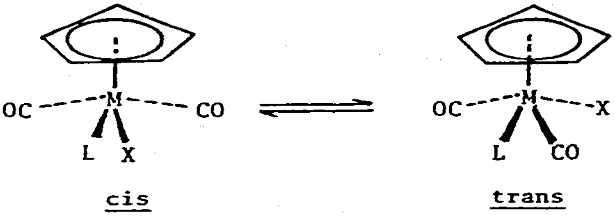
(10)

(NH$_2$ and OH protons in (A) and (B) can be deuterated with D$_2$O/THF)



(11)

A number of other studies of (η-cyclopentadienyl)carbonylmetal complexes have also been reported. Alway and Barnett have interconverted the linkage isomers of (η-Cp)Mo(CO)$_3$(CNS) <u>via</u> ultraviolet irradiation.[198] In addition, they have studied the photochemically-induced <u>cis</u>-<u>trans</u> isomerization (Eq. 12) of (η-Cp)M(CO)$_2$(PPh$_3$)(X) (M = Mo, W; X = Br, I) and the accompanying

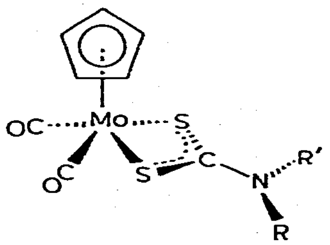


(12)

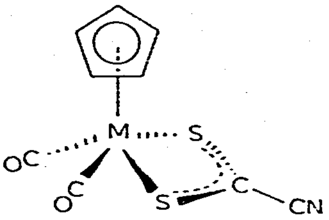
disproportionation of these complexes to $(\eta\text{-Cp})M(CO)(PPh_3)_2X$ and $(\eta\text{-Cp})M(CO)_3X$: dissociation of CO or PPh_3 may be an important path in the observed isomerizations.[198] Beach and Barnett have also reported on the separation (*via* column chromatography) of such isomers, $(\eta\text{-Cp})M(CO)_2(PPh_3)(X)$ (M = Mo, X = Br, I; M = W, X = I), which were prepared directly from $(\eta\text{-Cp})M(CO)_3X$ or through reaction of $(\eta\text{-Cp})M(CO)_2(PPh_3)(COCH_3)$ and X_2. The isomers are interconvertable at 80°, and the isomer ratios depend upon the preparative method employed.[199] Craig and Edwards have also discussed such isomers, of $(\eta\text{-Cp})Mo(CO)_2(PR_2R')(R'')$ (R'' = Me, Et; R, R' = Me, Et, Ph).[200] Low temperature proton NMR spectra indicate that only the *trans* isomers exist in solution. The stereochemistry, and the mechanism of the *cis*-*trans* isomerization are discussed.[200]

The Na/Hg reduction of $(\eta\text{-Cp})Mo(CO)_2(CNCH_3)(Cl)$ in THF at room temperature affords the $(\eta\text{-Cp})Mo(CO)_2(CNCH_3)^-$ anion, in which the isonitrile enters into appreciable π-backbonding with the metal.[201] The anion is a useful synthetic intermediate, reacting with CH_2ClCN, Me_3GeBr, Me_3SnCl and Ph_3PbI to afford the complexes $(\eta\text{-Cp})Mo(CO)_2(CNCH_3)R$ (R = CH_2CN, Me_3Ge, Me_3Sn and Ph_3Pb). Additionally, treatment of the anion with acetic acid affords the hydride, $(\eta\text{-Cp})Mo(CO)_2(CNCH_3)(H)$,[201] which decomposes at room temperature to afford $(\eta\text{-Cp})_2Mo_2(CO)_5(CNCH_3)$ (*AS* 1973/252) and $[(\eta\text{-Cp})Mo(CO)_3]_2$.

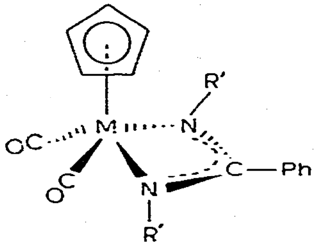
Reactions of $(\eta\text{-Cp})Mo(CO)_3Cl$ with dithiocarbamato complexes containing two different substituents on N in refluxing acetonitrile afford the complexes (LXXI, R = $CHMe_2$, CHMePh; R' = H) which are chiral, and were identified through use of low temperature ^1H NMR spectrometry.[202] Racemization at room temperature proceeds *via* rotation about the $S_2C\text{-}NR_2$ bond. Analogous reactions of the cyanodithioformate ion in acetone afford the violet complexes (LXXII, M = Mo, W) in which the substituent is superior to other dithio ligands in its π-accepting ability.[203] Related



(LXXI)

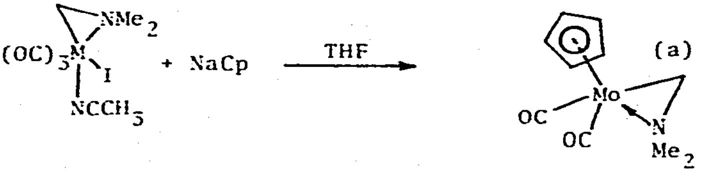


(LXXII)



(LXXIII)

complexes (LXXIII) have been prepared by Inglis, Kilner and coworkers,[204,205] via analogous methods from R'NC(R)NR'Li (M = Mo, W; R = Ph, R' = H, Ph or p-tolyl). Fong and Wilkinson have discussed reaction (13), and have prepared the related η^1-CH_2NMe

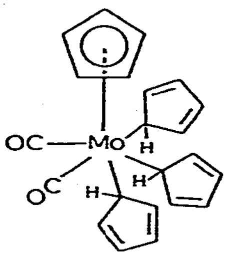


(13)

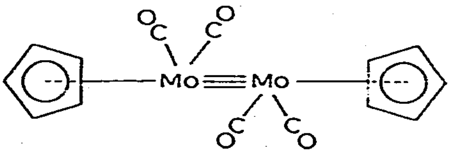
tricarbonyl complexes (M = Mo, W) through direct reaction of $Na[(\eta\text{-}Cp)M(CO)_3]$ and $Me_2\overset{+}{N}CH_2I^-$. For Mo but not W this complex loses CO to form (13a) upon heating in petroleum ether.[132] Herberhold and Bernhagen have reacted $(\eta\text{-}Cp)Cr(CO)_3^-$ with $[para\text{-}XC_6H_4N{\equiv}N^+]BF_4^-$, (X = OMe, Me, H, F, NO_2) in glacial acetic acid under nitrogen and have obtained $(\eta\text{-}Cp)Cr(CO)_2[N{=}N\text{-}C_6H_4X\text{-}para]$, in which the ligand functions as a three electron-donating group.[206] The reaction of $(\eta\text{-}Cp)Mo(CO)_2Cl_3$ with NaCp in $NaBH_4$/THF yields (LXXIV) as fairly air-stable, bright yellow crystals, and in which (proton NMR) the η^1-Cp rings do not undergo rapid 1,2-shifts.[207]

The $[(\eta\text{-}Cp)M(CO)_2RS]_2$ dimer (RS bridges, R = p-MeC_6H_4) adds CO in THF (but not in non-polar solvents) to yield $(\eta\text{-}Cp)M(CO)_3SR$ (M = Mo, W). The analogous complexes (R = Me) can also be obtained via reaction of $(\eta\text{-}Cp)M(CO)_3I$ and MeSK, and, upon heating, afford the dimeric species.[208] The mechanism of the reaction with CO is believed to proceed via initial bridge-opening.

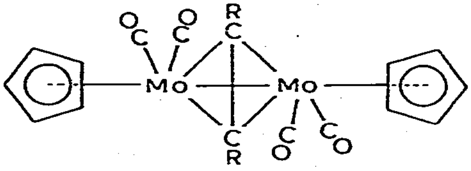
Other dimeric species, containing multiple Mo-Mo bonds, have also received attention. $(\eta\text{-}Cp)_2Mo_2(CO)_6$, upon heating, affords variable yields of $(\eta\text{-}Cp)_2Mo_2(CO)_4$ (LXXV), which reacts with PPh_3 or $P(OMe)_3$ (L) to afford $(\eta\text{-}Cp)(CO)_2(L)Mo\text{-}Mo(L)(CO)_3(\eta\text{-}Cp)$,



(LXXIV)



(LXXV)

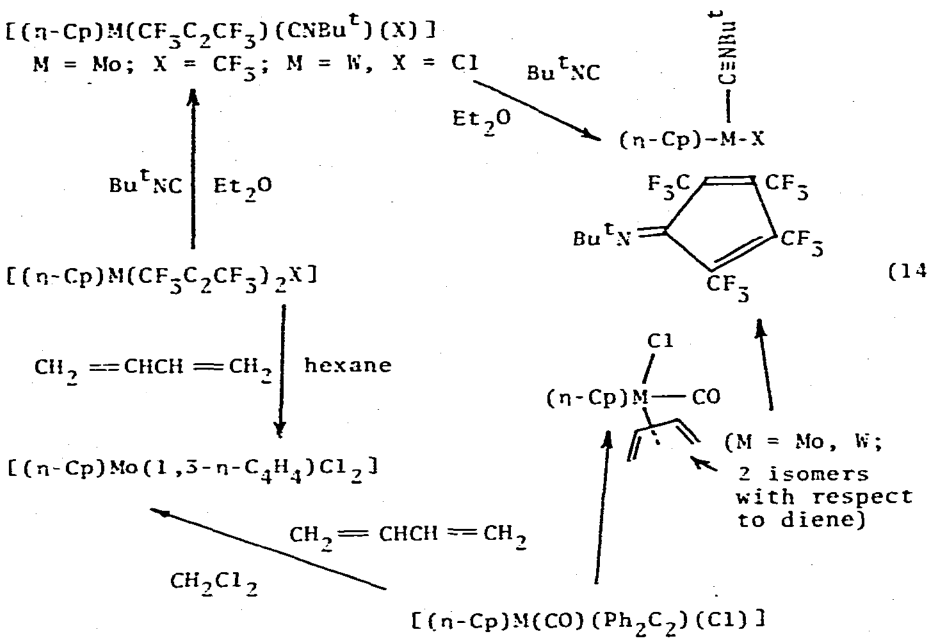


(LXXVI)

and with RC≡CR' (R = R' = H; R = Ph, R' = H) to yield red (LXXVI).[209] The complex (LXXV) has been shown, by X-ray analysis, to contain a Mo-Mo triple bond, and reacts with R_2S_2 or I_2 to yield $(\eta\text{-Cp})_2Mo_2(CO)_4I_2$ or $-R_2S_2$, which may alternately be formulated as containing a Mo=Mo double bond, or, for a "bridged" structure, no formal Mo-Mo bond.[209] (LXXV) or its $(\eta\text{-Me}_5Cp)$ analogue reversibly adds two moles of CO to afford the well-known $[(\eta\text{-Cp})Mo(CO)_3]_2$ dimer.[210]

The reaction of $(\eta\text{-Cp})Mo(CO)_3X$ (X = Cl, Br, I) with acetylenes has led to the formation of novel $(\eta\text{-Cp})Mo(RC{\equiv}CR)_2X$ complexes (R = Me, CF_3) in which the metal formally is two electrons short of the octadecet. Reaction of Ph_2C_2 with $(\eta\text{-Cp})Mo(CO)_3X$ affords $(\eta\text{-Cp})Mo(CO)(Ph_2C_2)X$ complexes, as well as the cyclobutadiene complex, $(\eta\text{-Cp})Mo(Ph_4C_4)(CO)Cl$.[211] The electron-deficient $(\eta\text{-Cp})Mo(CF_3C{\equiv}CCF_3)_2X$ species enter into a wide range of reactions, some of which are summarized in (14);[38] Its reaction with potassium tris(pyrazolyl) borate affords (V).[38]

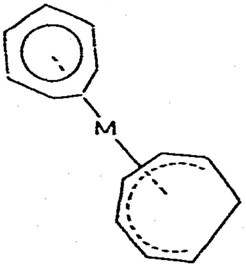
The co-condensation of cyclopentadiene and Mo or W atoms, or of cyclopentene with W atoms affords $(\eta\text{-Cp})_2MH_2$.[212] Use of a 5:1 ratio of benzene or toluene to cyclopentadiene yields



(14)

$(\eta\text{-}C_6H_6)(\eta\text{-}Cp)W\text{-}H$ or $(\eta\text{-}C_6H_5Me)(\eta\text{-}Cp)W\text{-}H$. Mo or W atoms co-condensed with 1,3,5-cycloheptatriene afford (LXXVII), in which the η^5 ring can be replaced employing refluxing THF/NaCp over 18 hr to yield $(\eta\text{-}C_7H_7)(\eta\text{-}Cp)Mo$.[212] Ultraviolet irradiation of $(\eta\text{-}Cp)_2WH_2$ in methanol affords $(\eta\text{-}Cp)_2W(H)(OMe)$ and $(\eta\text{-}Cp)_2W\text{-}(Me)(OMe)$, postulated to arise via the intermediacy of tungstenocene, a transition metal carbene analogue.[213]

Reactions of $(\eta\text{-}Cp)_2MH_2$ (M = Mo, W) with alkyl- and aryl derivatives of Li, Mg and Al to afford bis-(η-Cp) complexes



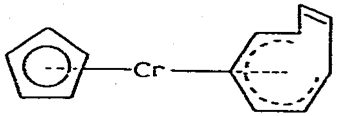
(LXXVII)

containing mixed metal-metal bonds have been studied. Thus reaction of $(\eta\text{-}Cp)_2MoH_2$ with Me_3Al affords $(\eta\text{-}Cp)_2Mo_2H_3Al_3Me_3$, of a 1:1 mixture of MeMgBr and $(\eta\text{-}Cp)_2WH_2$, $(\eta\text{-}Cp)_2WH_2MeMgBr$, and of $(\eta\text{-Cp})_2\text{MoH}_2$ with BuLi, $[(\eta\text{-Cp})_2\text{MoHLi}]_4$.[214] $(\eta\text{-Cp})_2\text{MCl}_2$ react with the Grignard reagents REMgBr to afford $(\eta\text{-Cp})_2\text{M(ER)}_2$ products (M = Mo, W; ER = SeMe, SePh, TePh, $\text{TeC}_6\text{H}_4\text{Me-}\underline{p}$. The complexes revert to the dichlorides upon treatment with concentrated HCl, and stabilities vary Se>Te.[215]

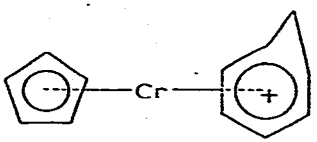
Reactions of $(\eta\text{-Cp})_2\text{Mo(O)Cl}_2$ or $(\eta\text{-indenyl})_2\text{Mo(O)Cl}_2$ with NaNO_2, AgNO_2 and AgNO_3 in THF afford $(\eta\text{-Cp})_2\text{Mo(O)(R)}_2$ or $(\eta\text{-indenyl})_2\text{Mo(O)(R)}_2$ products (R = NO_2, ONO, ONO_2), of which the ONO complexes are least stable, rearranging to the NO_2 isomers upon storage.[216] Reactions of $(\eta\text{-Cp})_2\text{W(O)Cl}_2$ with KR or AgR in refluxing THF afford $(\eta\text{-Cp})_2\text{W(O)(R)}_2$ products (R = CN, NC, NCO, OCN, NCS, SCN), characterized by IR spectra.[217] The condensation of (η-Cp)- or $(\eta\text{-indenyl})\text{Mo(O)Cl}_2$ with phenols (R(OH)_n, n = 1,2; R(OH)_n = phenol, α-, β-naphthol, resorcinol, catechol, phloroglucinol or pyrogallol) resulted in evolution of HCl and formation of (η-Cp)- or $(\eta\text{-C}_9\text{H}_7)\text{Mo(O)(O}_2\text{R)}$ and $\text{-(O}_2\text{R}_2)$ complexes, whose properties were studied.[218]

The reversible uptake of $(\eta\text{-Cp})_2\text{Cr}$ by CO in toluene to afford $(\eta\text{-Cp})_2\text{Cr(CO)}$ has been studied as a function of temperature and the equilibrium pressure of CO above the solutions, and values of ΔH^o (-18.8(5) $\text{kcal}\cdot\text{mole}^{-1}$) and ΔS^o (-60(2) $\text{cal}\cdot\text{deg}^{-1}\text{-mole}^{-1}$) for the process have been determined.[219] $(\eta\text{-Cp})_2\text{MCl}_2$ (M = Cr, Mo, W) react with sodium amalgam in the presence of CO and hydrogen to afford $(\eta\text{-Cp})(\eta^3\text{-C}_5\text{H}_7)\text{M(CO)}_2$ products; reaction of $(\eta\text{-Cp})_2\text{WCl}_2$ with CO at high pressure yields the blue $(\eta\text{-Cp})_2\text{W(CO)}_2$, in which W formally possesses 20 valence electrons.[219]

The reaction of $\text{CpCrCl}_2\cdot\text{THF}$ with cyclooctatetraene in the presence of Pr^iMgBr affords paramagnetic (LXXVIII), fluxional on the NMR time scale, which can be protonated employing HPF_6 to afford (LXXIX), formulated as containing the "homotropylium" ring system.[220] Complex (LXXIX) can undergo nucleophilic addition of R^- (= H^-, CH_3^-) through treatment with LiAlH_4 or MeLi to give 7-substituted 1,3,5-cyclooctatriene derivatives, $(\eta\text{-Cp})\text{Cr}^{\text{I}}\text{-}(7\text{-R-}1,3,5\text{-COT})$.[220]



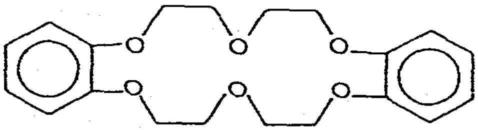
(LXXVIII)



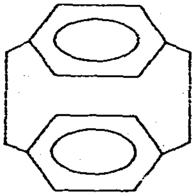
(LXXIX)

Green and coworkers have studied reactions of $[(\eta\text{-}C_6H_6)Mo\text{-}(\eta\text{-}C_3H_5)Cl]_2$ with cyclopentene in the presence of $EtAlCl_3$, which afford a brown oil which yields $(\eta\text{-}Cp)(\eta\text{-}C_6H_6)Mo$ upon treatment with alkaline sodium dithionite, and $(\eta\text{-}Cp)(\eta\text{-}C_6H_6)MoCl$ upon reaction with LiCl in methanol. The latter complex can be converted to the iodide analogue through treatment with I_2.[221]

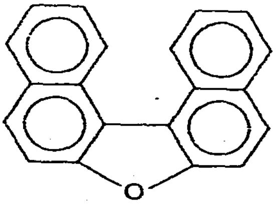
The synthesis of a variety of $(\eta\text{-arene})M(CO)_3$ complexes and their simple substitution products has been reported. Thus Cho and Fernandez have prepared thermally from the hexacarbonyl such chromium complexes for (arene) = *o*, *m*-, *p*-phenylenediamine, 2,4- and 2,6-diaminotoluene, and N,N-diphenyl-*p*-phenylenediamine.[222] Pannell and coworkers have prepared (photochemically) derivatives of dibenzo-18-crown-6 (LXXX) in which the $-Cr(CO)_3$ moieties are attached to one or both arene rings.[223] In these complexes, the ability of the crown ether to extract alkali metal salts into organic solvents is decreased, and, for the disubstituted ether, the order of selectivity is reversed for Na^+ and K^+. This observation is attributed to withdrawal of electron density from the oxygen crown by the $-Cr(CO)_3$ substituents.[223] The photochemical production of $(22\text{-cy})M(CO)_3$ complexes (22-cy = 2,2-paracyclophane, (LXXXI, M = Cr, Mo, W) has been reported. Bonding has been discussed on the basis of IR, ^1H nmr and mass spectra. The Mo complex, which is the least stable, decomposes *via* a first-order rate law.[224] Frauendorfer and coworkers have prepared tricarbonylchromium derivatives of the six possible isomeric forms of dinaphthofuran, one of which, dinaphtho[2,1-b:1',2'-d]furan is shown in (LXXXII). For (LXXXII), complexes



(LXXX)



(LXXXI)

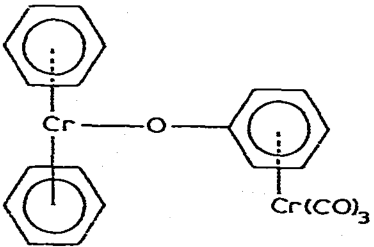


(LXXXII)

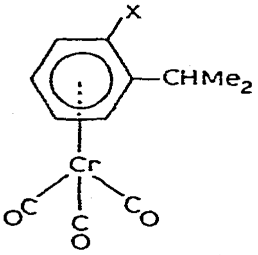
in which $-Cr(CO)_3$ groups are attached to either or both terminal ring of the naphthalene systems were obtained; for the other isomeric dinaphthofurans, where it was possible to determine, attachment is also to the terminal rings; steric factors dictate whether or not a second $-Cr(CO)_3$ will bond. The complexes were characterized through use of IR, ^1H nmr and mass spectral data.[225]

Petukhov have prepared (LXXXIII) through reaction of $(\eta-C_6H_6)_2Cr(OH)$ and $(\eta-HOC_6H_5)Cr(CO)_3$ at room temperature. The complex decomposes thermally to afford $Cr(CO)_6$, $(\eta-C_6H_6)_2Cr$, $Cr(OPh)_2$ and C_6H_6.[226]

A general preparative procedure for synthesis of $(\eta$-arene$)$-$Mo(CO)_3$ complexes, through which some thirty such complexes, many previously unreported, have been prepared, involves reaction of cis-(pyridine)$_3$Mo(CO)$_3$ and the appropriate arene in the presence of boron trifluoride etherate at room temperature. This method is not favored, however, for Cr and W. For this reaction, where trans-stilbene and 1,4-diphenylbutadiene were the arenes employed, both mono- and dinuclear products were obtained. Direct reaction of 1,4-diphenylbutadiene with $Mo(CO)_6$ or $W(CO)_6$ in contrast, leads to formation of the (trans-1,4-diphenylbutadiene)$_2$M(CO)$_2$ complexes bonded through the butadiene functionality. For tolan, an unstable π-complex was obtained, but $(PhCCPh)_3Mo(CO)$ was the main product.[227] This general method has also been employed to prepare a series of $(\eta$-thiophene$)Cr(CO)_3$ complexes. Tris(pyridine)$Cr(CO)_3$ reacts with the appropriate thiophene $1,2-XYC_4H_2S$ (X = OMe, Me, H, Br, COOMe; Y = H and X = H; Y = OMe, Me, Br, COOMe) in ethereal boron trifluoride etherate.[228] Öfele and associates have prepared other tricarbonyl chromium complexes of heterocyclic ligands, $(\eta-Me_5py)Cr(CO)_3$ and $(\eta-2,4,6-Me_3py)Cr(CO)_3$, directly, in boiling dioxane. The complexes were characterized employing an X-ray structural determination, and infrared and proton NMR spectra.[229]

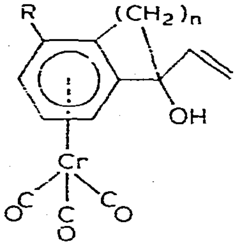


(LXXXIII)

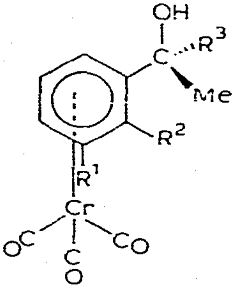


(LXXXIV)

Ligand-exchange of the (η-arene) groups is also developing as a useful preparative procedure. The complexes (LXXXIV), (X = NH_2, NMe_2, OMe) have been synthesized through a sealed tube reaction (neat) of $(\eta\text{-}C_6H_6)Cr(CO)_3$ with the appropriate arene.[230] A similar exchange process has been employed for reaction of (LXXXV) (n = 2,3, R = H, OMe) with 1,2,3-$R^1R^2R^3C_6H_3$ complexes (R^1, R^2, R^3 given: OMe, H, CO_2Me; NMe_2, H, CO_2Me; Me, H, NH_2; NH_2, Me, H; Me, Me, H). The key to this procedure lies in stabilization of a carbonium ion adjacent to the complexed ring through use of a tertiary alcoholic function. Reactions of (LXXXVI a-c) (a: R^1, R^2, R^3 = H, Me, $-CH=CH_2$; b: H, Me, Ph; c: Me, H, Ph) with 1,2,3-$(R^1R^2R^3C_6H_3)$, (R^1, R^2, R^3 = H, Me, NH_2 (LXXXVI-a,b); Me, H, NH_2; CO_2Me, H, NMe_2; OMe, $-(CH_2)_3-$C(O)- (LXXXVI-c), which also utilized this principle, were also carried out.[231]



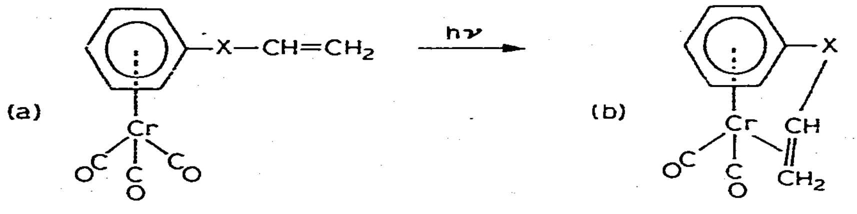
(LXXXV)



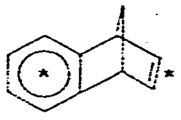
(LXXXVI)

Meyer and Jaouen have also effected arene-exchange for $(\eta\text{-arene})Cr(CO)_3$ complexes containing tertiary alcoholic functionalities (arene = 1-exo-phenyl-1-endo-tetralol, 1-exo-vinyl-1-endo-tetralol), and methylphenyl-o-methylbenchotrenylmethanol. Among the complexes (prepared in 17-86% yield) are those for which the η-arene ligands are (those directly prepared for the first time marked with asterisk): 2-aminotoluene, 3-aminotoluene, 2-aminobenzoic acid methyl ester, 3-aminobenzoic methyl ester, 2-methoxyaniline, benzoic acid methyl ester, *4-methylbenzaldehyde, *4-aminobenzonitrile, 4-methoxyaniline and 3-dimethylaminobenzoic acid methyl ester. The lack of asymmetric synthesis observed (confirmed through reaction of several of the products with optically-active reagents) supports liberation of $-Cr(CO)_3$, rather than a bimolecular reaction path.[232]

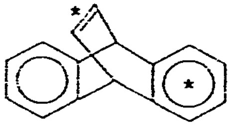
Also synthesized and investigated have been $(\eta\text{-arene})Cr(CO)_3$ complexes in which, as a result of the presence of a pendant olefinic functionality on the arene ring, the arene can function as a bidentate chelating ligand. Ring-closure is generally effected through ultraviolet irradiation of the (η-arene)Cr(CO)$_3$ complex. Thus Nesmeyanov and coworkers have prepared (direct synthesis) the complexes (LXXXVII-a), which afford the species (LXXXVII-b) upon irradiation (X = CH$_2$, OCH$_2$, (CH$_2$)$_2$, (CH$_2$)$_3$, (CH$_2$)$_4$).[233] Trahanovsky and Hall have studied related systems employing proton NMR spectra as the principal diagnostic tool. The ligands which give dicarbonylchromium chelated complexes upon irradiation include (LXXXVIII and LXXXIX, points of attachment marked by asterisk), Ph(CH$_2$)$_n$CH=CH$_2$ (n = 2,3), PhCD$_2$CH$_2$CH=CH$_2$, PhOCH$_2$CH=CH$_2$, PhCH$_2$OCH=CH$_2$. Tricarbonyl complexes which did not enter into ring-closure upon irradiation include those in which the (η-arene) ligands included (XC and XCI) as well as Ph(CH$_2$)$_n$CH=CH$_2$ (n = 1,4), and PhCH$_2$OCOCH=CH$_2$.[234] Howell and



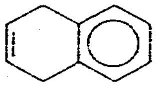
(LXXXVII)



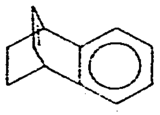
(LXXXVIII)



(LXXXIX)



(XC)

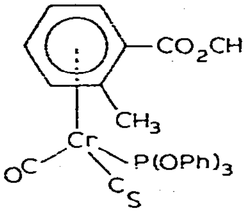


(XCI)

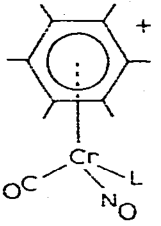
Trahanovsky have studied the Lewis base-promoted ring-opening of the dicarbonylchromium complex of (LXXXVIII) to afford the (η-arene)Cr(CO)$_2$(L) products.[235] Only for L which are considered to be good π-acceptors (= RNC (R = Me, Bu^t, cyclohexyl), MeC(CH$_2$O)$_3$P, As(OMe)$_3$, PF$_3$, P(OMe)$_3$ and PPh$_3$) was the olefinic group displaced. For other ligands investigated (Me$_3$N, py, MeCN, PhSMe, THF, cyclopentene, MeOH), no displacement was noted at room temperature over 80 or more hours. These results may be contrasted to those observed for non-clelating complexes of the type (η-arene)Cr(CO)$_2$(π-olefin), in which the olefin was readily displaced by a variety of nucleophiles.[236] The difference was attributed to a chelate effect; it was not possible, on the basis of the study, to distinguish between a ring-opening mechanism, and one involving nucleophilic attack at Cr.[235]

The first reported resolution of chromium(0) chiral centers has been effected through synthesis of (LCII) through use of known synthetic procedures from the tricarbonylchromium precursor, resolution of the enantiomers, and removal of the CO_2Me functionality through $LiAlH_4/AlCl_3$ reduction, to destroy ring chirality. Chiral chromium complexes, analogous, but with L = PPh_3 or $P(OEt)_3$ rather than $P(OPh)_3$, were also prepared, although in lower optical purity.[237-238]

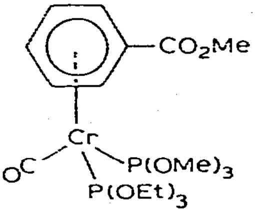
Other complexes *e. g.*, (XCIII, L = $P(OMe)_3$, $P(OEt)_3$, PMe_2Ph, diphos), synthesized *via* nitrosylation followed by CO-replacement by L, and (XCIV), also containing chiral Cr centers, were not resolved.[237] The complexes (XCIII) also have been prepared by



(XCII)

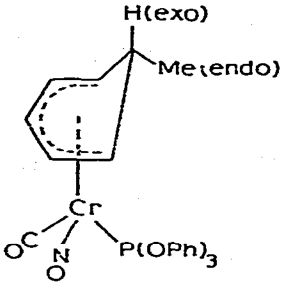


(XCIII)

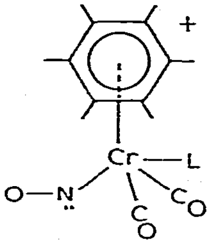


(XCIV)

Connelly and coworkers *via* reaction of $NOPF_6$ with $(\eta\text{-}Me_6C_6)Cr(CO)_2(L)$ (L = PPh_3, PMe_2Ph, $P(OPh)_3$, $P(OMe)_3$).[239] The $NaBH_4$ reduction of these complexes gave (XCV), containing an *exo* proton. Reaction of the $(\eta\text{-}Me_6C_6)Cr(CO)_2(L)$ complexes with PhN_2PF_6, in contrast, affords paramagnetic $[(\eta\text{-}Me_6C_6)Cr(CO)_2(L)]^+$ (L = PPh_3, $PMePh_2$, PMe_2Ph), or $[(\eta\text{-}Me_6C_6)Cr(CO)_2(L)]^+$ and $[(\eta\text{-}Me_6C_6)Cr(CO)_2(PhN_2)]^+$ (L = $P(OMe)_3$, $P(OPh)_3$). Electrochemical studies reveal that oxidation of $[(\eta\text{-}Me_6C_6)Cr(CO)_2(L)]$ to $[(\eta\text{-}Me_6C_6)Cr(CO)_2(L)]^{+\cdot}$ is a reversible, one-step process. An overall mechanism for the chemical process involving initial nucleophilic attack at $(\eta\text{-}Me_6C_6)Cr(CO)_2(L)$ by NO^+ or PhN_2^+, affording a species which, for NO, for example (XCVI), contains the "bent" NO^- ligand, and which then dissociates CO, L or NO was discussed. The differing chemical behavior of NO^+ and PhN_2^+ depends upon the greater ease of one-electron oxidation by PhN_2^+ than by NO^+, which results in alteration of relative Cr-N, Cr-C and Cr-L bond-strengths in the intermediates (XCVI) for the two substituents.[239] Connelly and Johnson have also studied the chemical and electrochemical oxidation of $(\eta\text{-}C_6Me_{6-n}H_n)Cr(CO)_2(acetylene)$ (n = 0,1; acetylene = PhCCPh, *p*-$MeOC_6H_4CCC_6H_4OMe$-*p*, prepared *via* ultraviolet irradiation of



(XCV)



(XCVI)

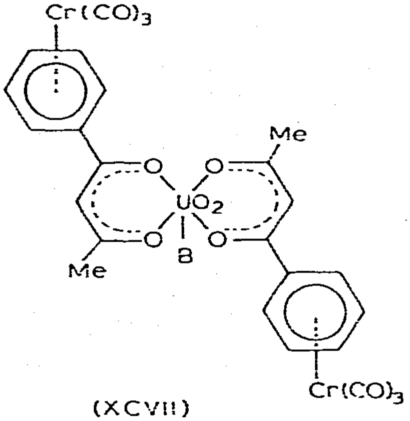
the acetylene and appropriate tricarbonylchromium complex. The acetylenic complexes are oxidized to the maroon monocations by NO^+, Ag^+ or I_2, and electrochemical and ESR data for the species are reported.[240]

Synthesis of the red selenocarbonyl, $(\eta\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$ has been effected through reaction of CSe_2 with $(\eta\text{-}C_6H_5CO_2Me)Cr(CO)_2(THF)$. The latter complex was prepared in turn through uv irradiation of the corresponding tricarbonyl. The complex was characterized through infrared, Raman and mass spectra; the possibility of a Cr-Se-C linkage cannot be ruled out.[241]

The formation of charge-transfer complexes formed between $(\eta\text{-arene})Cr(CO)_3$ species and acceptor ligands such as $HgCl_2$ (with $(\eta\text{-}C_6H_6)Cr(CO)_3$) or maleic anhydride (with $(\eta\text{-}C_6H_5NH_2)Cr(CO)_3$) has been studied by Magomedov and coworkers,[242] while Lokshin and collaborators have investigated the interaction of several $(\eta\text{-arene})M(CO)_3$ complexes and related species (arene = C_6H_6, M = Cr, W; 1,3,5-$Me_3C_6H_3$, Cr, Mo; Me_6C_6, Cr, and $(\eta\text{-}C_6H_6)Cr(CO)_2(PPh_3)$) with $AlCl_3$ in benzene and CH_2Cl_2.[243] Interaction at both a carbonyl oxygen and the metal atom was observed, and these infrared studies revealed solvent, structural and electronic influences on the site of interations. Thus, interaction at the carbonyl was favored in benzene _vs._ CH_2Cl_2 and in the dicarbonyl complex _vs._ the tricarbonyls, but interaction at the metal was favored by electron-releasing substituents on the arene ring.[243]

Castellato, Vigato and Vidali have prepared complexes of the type UO_2L_2L' through reaction of $(\eta\text{-}XC_6H_5)Cr(CO)_3$ (= LH; X = COOH, $COCH_2COCH_3$) with methanolic sodium hydroxide, followed by displacement of methanol (= L') by treatment with other L' (Me_2SO, Ph_3PO, Bu_3PO). Formulation of the complexes, analogous both for the benzoate and benzoyl acetonate products (XCVII) envisions pentagonal bipyramidal geometry about uranium.[244]

Seyferth and Eschback have prepared the royal blue stable carbonium ion salt (XCVIII), the first bearing adjacent $-Cr(CO)_3$ groups, from $Hg[(\eta-C_6H_5)Cr(CO)_3]_2$ (prepared directly from $Cr(CO)_6$ and Ph_2Hg). Conversion of the -Hg- functionality to $-\overset{+}{C}H-$ involved treatment with $Co_2(CO)_8$ in THF (conversion of -Hg- to -C(O)-), reduction with $NaBH_4$/MeOH to afford -CH(OH)-, and further reaction with HPF_6 in acetic acid to afford (XCVIII). The salt reacts to form the -CH(OEt)-, $-CH(NEt_2)-$ and $-CH(2-C_4H_4N)-$ functionalities with ethanol, diethylamine or pyrrole, respectively, and thus is a useful intermediate for the synthesis of $(\eta$-arene$)Cr(CO)_3$ complexes containing unusual ring substituents.[245]



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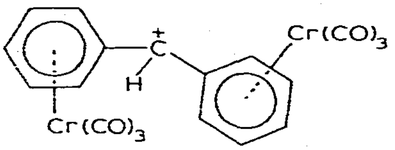
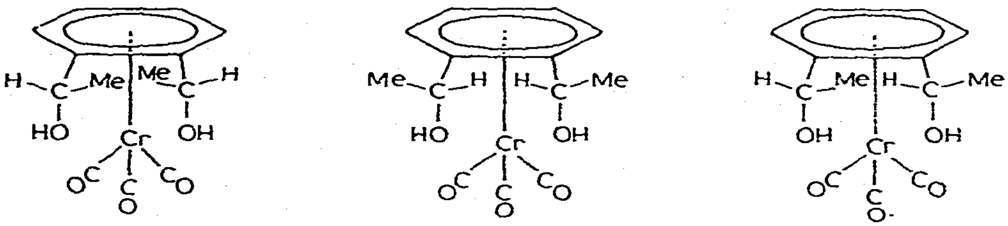


(XCVIII)

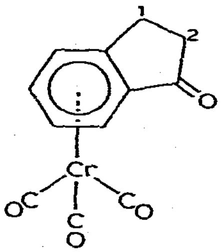
Other studies which involve transformation of the arene function in their carbonylmetal π-complexes have also been discussed. Jaouen and coworkers have studied the influence of $-Cr(CO)_2L$ substituents on the ease of alkylation of complexed PhCOMe or $PhCH_2CO_2Me$. The activating power decreases in the order $Cr(CO)_2CS > Cr(CO)_3 > Cr(CO)_2P(OPh)_3 > Cr(CO)_2PPh_3$, with the last-named moiety protecting the ring substituent from alkylation. The studies indicate that the appropriate π-complexed $Cr(CO)_2L$ moiety can activate, protect or enhance selectivity of ring substituents to alkylation.[246] Semmelhack and coworkers have found that complexation of C_6H_6 to the $-Cr(CO)_3$ moiety increases ring susceptibility to nucleophilic attack. Thus $(\eta-C_6H_6)Cr(CO)_3$ undergoes "nucleophilic aromatic substitution for hydride" through reaction with R^- (from LiR, BrMgR and KR). The free arene can be obtained, often in >90 per cent yield, through treatment of the resulting $(\eta-C_6H_5R)Cr(CO)_3$ complex with I_2 at room temperature.[247]

There is continued interest in the stereochemistry of arenes bonded to Group VI-B metal tricarbonyls. Besançon and coworkers have prepared the three stereoisomeric o-substituted glycols, (XCIX) from (η-o-$(CHO)_2C_6H_4)Cr(CO)_3$ (via reaction with methylmagnesium iodide) and (η-o-$(MeOC)_2C_6H_4)Cr(CO)_3$ (via reduction with KBH_4). They were identified via chemical derivatization and proton and ^{13}C NMR spectroscopy. The two corresponding uncomplexed alcohols were obtained through photochemical decomposition of the arenetricarbonylchromium complexes. The observed stereoselectivity for formation of the mixtures of the three benchotrenes was discussed.[248] Jaouen and associates have studied the isomer distribution obtained through the phosphoric-acid cyclization of $(\eta\text{-}C_6H_5CHCH_3CH_2COOH)Cr(CO)_3$ (a) and $(\eta\text{-}C_6H_5CH_2CHCH_3COOH)Cr(CO)_3$ (b), which afforded (C), containing CH_3 and H bonded to the carbons labeled 1 and 2, respectively, via NMR. The observed differences were attributed to the proximity of the methyl group in reaction (a) to the Cr atom.[249] Jaouen and Meyer have also reported the facile syntheses of optically-active 2-substituted indanones, indanols, tetralones and tetralols via initial synthesis, resolution into the optically pure forms, and determination of the absolute configurations of (η-1-indanone)-



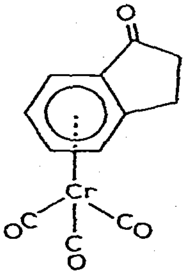
meso meso racemic

(XCIX)

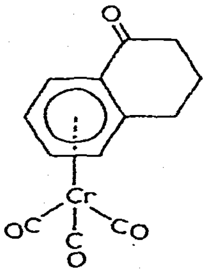


(a) Me,H at C^1
(b) Me,H at C^2

(C)

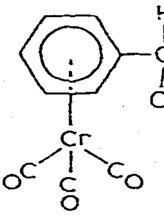


(CI)

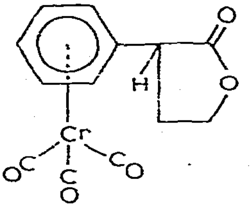


(CII)

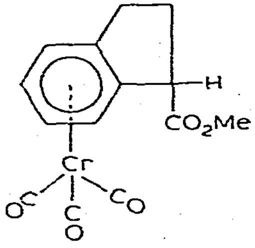
$Cr(CO)_3$ and (η-1-tetralone)$Cr(CO)_3$ (CI-CII). These complexes have served as starting materials for the stereospecific synthesis of chiral arene complexes, e. g., 2-methyl-1-indanone, 2-methyl-1-tetralone, cis- and trans-2-methyl-1-indanols, and cis- and trans-2-methyl-1-tetralols. The arenes are difficult or impossible to synthesize by other methods.[250] Also reported have been the stereospecific reduction of various (η-indanone)-$Cr(CO)_3$ complexes employing KBH_4, which afford exclusively the (η-endo-1-indanol)$Cr(CO)_3$ species. Prepared in this manner were (η-exo-3-methyl-endo-1-indanol)$Cr(CO)_3$, (η-endo-3-methyl-endo-1-indanol)$Cr(CO)_3$, and the corresponding 2-methyl-1-indanol complexes.[251] Boudeville and des Abbayes have studied the alkylation of (CIII-CV) at the proton shown via NaH/DMF or phase transfer catalysis with RX (R = Me, X = I; R = $PhCH_2$, $CH_2{=}CHCH_2$, $CHC{\equiv}CCH_2$, CH_2CO_2Me; X = Br). The complexation of the arenes with the



(CIII)



(CIV)



(CV)

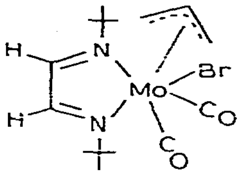
tricarbonylchromium moiety augments the acidity of the protons, facilitating alkylation, and it is proposed that the rigorously exo stereochemistry observed for R arises as the result of intramolecular interactions of the ester functions with the tricarbonylchromium groups.[252]

Miscellaneous physical studies employing (η-arene)$Cr(CO)_3$ complexes have also been reported. Neuse has reported correlations between the substituent parameters σ_I, σ_p, σ^{o}_{p}, σ^{p}_{R} and σ^{o}_{R} with carbonyl stretching force constants, k(CO), for twenty-eight poly- and mono-ring-substituted (η-arene)$Cr(CO)_3$ complexes. The results indicate that electronic effects of substituents are both mesomeric (dominant) and inductive, and that there is appreciable participation of the ring carbon σ-framework in bond formation with the metal.[253] Gubin and coworkers have reported the ionization constants for C_6H_5-C_6H_4OH-β, and C_6H_5-$C_6H_4NH_3^+$-β and their tricarbonylchromium complexes (metal bonded to unsubstituted phenyl ring). The tricarbonylchromium complexes were found to be a stronger acid, and weaker base, respectively, than the parent biphenyls. Calculated values of σ_p^-, σ_R^- and $\Delta\sigma_R^-$ for the $(\eta\text{-}C_6H_5\text{-})Cr(CO)_3$ moiety were discussed, as were the effects of substituents in monosubstituted biphenyls on the relative isomer distribution observed for the Nicholls-Whiting synthesis of $(\eta\text{-arene})Cr(CO)_3$ complexes.[254]

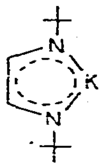
Again this year there have been reports of the synthesis and separation of $(\eta\text{-arene})_2Cr$ and related complexes. The chromium atom co-condensation of C_6H_5F, *m*-$C_6H_4(CF_3)_2$, *p*-$C_6H_4(CF_3)_2$ and *o*-$C_6H_4(Cl)(CF_3)$ have afforded the corresponding $(\eta\text{-arene})_2Cr$ complexes.[255] While these complexes exhibit striking stability, infrared evidence indicates that Cr-ring bonding is weaker in $(\eta\text{-}p\text{-}C_6H_4(CF_3)_2)_2Cr$ than in $(\eta\text{-}C_6H_6)_2Cr$. Direct co-condensation of Cr atoms and C_6H_5COOEt affords the expected symmetrical $(\eta\text{-}C_6H_5COOEt)_2Cr$, characterized, and studied, by mass spectrometry, differential thermal analysis, infrared and electronic spectra, polarography and esr.[256] The metallation of $(\eta\text{-}C_6H_6)_2Cr$ employing butyllithium in N,N,N',N'-tetramethylethylenediamine, followed by formylation with dimethylformamide has afforded $(\eta\text{-benzaldehyde})_2$-Cr, and $(\eta\text{-}C_6H_6)(\eta\text{-benzaldehyde})Cr$.[257]

The separation of mixtures of $(\eta\text{-arene})_2CrI$ complexes by column chromatography[258] and thin layer chromatography[259] has been reported, and a chromatographic system with circulating He carrier to inhibit decomposition has been employed to separate the products of synthesis of $(\eta\text{-}Pr^iC_6H_5)_2Cr$ at 200^o.[260]

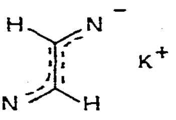
Brisdon and Griffin have prepared a variety of new complexes containing the η-allyl ligand. The complexes $(\eta\text{-}C_3H_5)M(CO)_2(L)_2(X)$ ($M = Mo, W$; L_2 = dipy, di(2-pyridyl)amine; X = Cl, Br, I, NCS, $MeCO_2$, CF_3CO_2, $PhSO_2$, *p*-$MeC_6H_4SO_2$) were prepared *via* one or more of four preparative procedures: (a) from the hexacarbonyl ($M(CO)_6$, allyl bromide and di(2-pyridyl)amine in refluxing THF); (b) from $L_2M(CO)_4$ complexes ((di(2-pyridyl)amine)$Mo(CO)_4$ and allyl isothiocyanate in refluxing THF); (c) anion-exchange ($(\eta\text{-}C_3H_5)Mo(CO)_2$-(dipy)(Cl) and NaO_2CCF_3 in acetone at room temperature); (d) from the $M(CO)_3(L_2)X^-$ anions ($[Ph_4P^+][W(CO)_3(dipy)(Br)^-]$ and allyl bromide in methanol at room temperature). In these complexes the oxo anions function as O-bonding, unidentate ligands. The reaction of three-electron donating anions (pentane-2,4-dienoate, diethyldithiocarbamate) (= A) and pyridine with these complexes results in displacement of halide and L_2 to afford $(\eta\text{-}C_3H_5)M(CO)_2$-(py)(A) products. In contrast, an analogous reaction with the salicylaldehyde anion afforded $(\eta\text{-}C_3H_5)Mo(CO)_2(dipy)(sal)$ in which sal functions as a monodentate ligand. The complexes were characterized by infrared and proton NMR spectra.[261] The reaction of (CVI) with solvated electrons (K) affords (CVII), while analogous reaction of the uncomplexed 1,4-dialkyl-1,4-diazabutadiene affords (CVIII); thus the conformation of the reduced species can be fixed at will.[262]



(CVI)



(CVII)



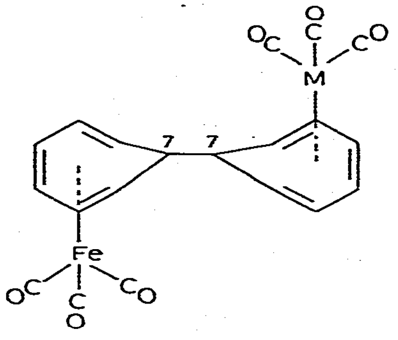
(CVIII)

Platbrood and Wilputte-Steinert, in a study of the photochemical reaction of $(NBD)Cr(CO)_4$ with PPh_3 which affords, ultimately, trans-$(PPh_3)_2Cr(CO)_4$, isolated an intermediate which evidence (^{13}C NMR, IR) indicates to be cis-$(\eta\text{-}NBD)(PPh_3)Cr(CO)_3$. Preliminary photochemical results were also discussed.[263]

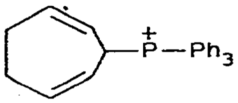
Ziegler and coworkers have synthesized $(\eta\text{-}1\text{-}6\text{-}7\text{-}Bu^tC_7H_7)$-$Mo(CO)_3$ through reaction of $(\eta\text{-}C_7H_7)Mo(CO)_2X$ and Bu^tMgBr or Na/Bu^tBr, or through treatment of $[(\eta\text{-}C_7H_7)Mo(CO)_3{}^+][BF_4{}^-]$ with Bu^tMgBr.[264] In all cases, the yield was low. The reaction of $(\eta\text{-}C_7H_7)Fe(CO)_3{}^-$ and $(\eta\text{-}C_7H_7)M(CO)_3{}^+$ (M = Cr, Mo, W) affords (CIX), in which an exo configuration of H(7) is postulated.[265]

Salzer and Werner have investigated reactions of $(\eta^6\text{-}C_7H_8)$-$M(CO)_3$ complexes with a variety of reagents.[266,267] For M = W, reaction of this complex with HCl affords $(\eta^5\text{-}C_7H_9)W(CO)_3Cl$, while its reaction with HBF_4/propionic anhydride gives $(\eta^5\text{-}C_7H_9)W(CO)_3{}^+$, highly solvated in solution.[266] This species reacts with Lewis bases (L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$) to afford $(\eta^5\text{-}C_7H_9)W(CO)_3L^+$, isolated as the $BF_4{}^-$ salts. With L_2 = diphos, the binuclear $(diphos)[(\eta^5\text{-}C_7H_9)W(CO)_3]_2{}^{2+}$ is obtained. These first cycloheptadienyltungsten complexes were characterized by infrared and ^1H NMR spectroscopy.[266] Reaction of $(\eta^6\text{-}C_7H_8)Mo(CO)_3$ with HBF_4 or HCl affords analogous $(\eta^5\text{-}C_7H_9)$-$Mo(CO)_3{}^+$ cations; however, further reaction with triphenylphosphine results in nucleophilic addition of PPh_3 at the ring with expulsion of the $[Mo(CO)_3]$ moiety to afford the phosphonium salt (CX), characterized by its proton-decoupled ^{13}C NMR spectrum.[267]

These results may be compared to those of Isaacs and Graham,[268] and Hackett and Jaouen[269] in studies of the $(\eta\text{-}C_7H_7)M(CO)_3{}^+$ cations in their reactions with Lewis bases. For M = Mo, the $(\eta\text{-}C_7H_7)Mo$-



(CIX)

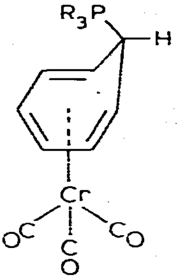


(CX)

$(CO)_2(L)^+$ cations (L = $P(OPh)_3$, PPh_3, PPh_2Me, $PPhMe_2$, $AsPh_3$), isolated as the PF_6 salts, are produced. These can be reduced to the neutral $(\eta^6\text{-}C_7H_8)Mo(CO)_2(L)$ species upon treatment with $NaBH_4$.[268] Similar reactions of $[(\eta\text{-}C_7H_7)Cr(CO)_3{}^+]\ BF_4{}^-$ with L (= PEt_2Ph, PBu_3), and, partially (equilibration) with PPh_3 affords (CXI), in which the PR_3 group is *exo*. The contrasting behavior of Cr and Mo was attributed to a more electrophilic ring system for Cr (see, however, ref. 305).[269] The convenient synthesis of $(\eta\text{-}C_7H_7)Mo(CO)_2(MR_3)$ complexes (M = Si, R = Cl; M = Ge, R = Cl, F, Ph; M = Sn, R = Cl, Ph) through Na/Hg reduction of $(\eta\text{-}C_7H_7)$-$Mo(CO)_2(Cl)$ in THF to afford the $(\eta\text{-}C_7H_7)Mo(CO)_2{}^-$ anions, and further treatment with Ph_3MCl (M = Ge, Sn), or direct reaction of $HSiCl_3$, in the presence of NEt_3, or of $HGeCl_3$ or $SnCl_2$ with $(\eta\text{-}C_7H_7)Mo(CO)_2Cl$ has been described. The fluoro complex was obtained through treatment of $(\eta\text{-}C_7H_7)Mo(CO)_2(GeCl_3)$ with $AgBR_4$.[270]

M. L. H. Green and coworkers have studied the sandwich complexes $[(\eta\text{-}C_7H_7)Mo(\eta\text{-arene})^+]PF_6{}^-$, which undergo displacement of the arene group and which thus provide a convenient entree into the synthesis of a variety of new complexes. Prepared were $[(\eta\text{-}C_7H_7)(\eta\text{-}C_6H_5R)Mo^+]\ PF_6{}^-$ (R = H, Me), from $[(\eta\text{-}C_7H_7)Mo(\pi\text{-}CH_3\text{-}CH{=}CH_2)Cl]_2$. The arene substituent in the products can be displaced by L (= MeCN, $PPhMe_2$, PPh_2Me) to afford $[(\eta\text{-}C_7H_7)MoL_3{}^+]$-$PF_6{}^-$ species. One of these reacts, in turn, with CO to produce $[(\eta\text{-}C_7H_7)Mo(PPh_2Me)_2(CO)^+]\ PF_6{}^-$. Treatment of $[(\eta\text{-}C_7H_7)(\eta\text{-}C_6H_5R)$-$Mo^+]\ PF_6{}^-$ with anions resulted in displacement of the arene, or attack at the arene ligand. Thus, the reaction of this complex with $BH_4{}^-$ afforded $[(\eta\text{-}C_7H_7)(\eta^5\text{-}C_6H_7)Mo]$, with sodium acetylacetonate and PPh_3 yielded $[(\eta\text{-}C_7H_7)Mo(PPh_3)(acac)]$, and with ethanol or methanol gave $[(\eta\text{-}C_7H_7)_2Mo_2(OR)_3{}^+]\ PF_6{}^-$. The reaction to give $(\eta\text{-}C_7H_7)Mo(PPh_3)(acac)$ is reversible, and thus $[(\eta\text{-}C_7H_7)(\eta\text{-arene})$-

Mo^+] products (arene = C_6H_6, 1,3,5-$Me_3C_6H_3$) are obtained through its treatment with the appropriate arene.[271]

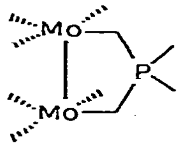


(CXI)

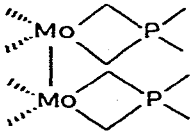
Metal-alkyl, -aryl and -hydride complexes. Hydrido, alkyl and aryl organometallic species are discussed in several places within this survey, where more appropriate. Other studies have also been reported. Casey and coworkers have reported the formation of yellow $Et_4N^+[W(CO)_5R^-]$ complexes formed either through reaction of $Et_4N^+[W(CO)_5Br^-]$ with RLi complexes in THF (R = Me, Ph, $PhCH_2$) or through photolysis of $Et_4N^+[W(CO)_5COR^-]$ complexes (R = Me, $PhCH_2$, p-xylyl). Reaction of the methyl and phenyl complexes with bases (L = CO, PPh_3) affords the carbonyl insertion products, cis - $W(CO)_4(L)(COR)$; for R = $PhCH_2$, no insertion products were formed.[272] Casey's group has also effected the direct methyl transfer from Mo to W through reaction of (η-Cp)$Mo(CO)_3Me$ and (η-Cp)$W(CO)_3^-$; the methyl in (η-Cp)$M(CO)_3Me$ (M = Mo, W) can also be transferred to Fe through reaction with (η-Cp)$Fe(CO)_2^-$, though not with $Mn(CO)_5^-$ or $Re(CO)_5^-$.[273]

The photochemical reaction of $(\eta\text{-Cp})_2WH_2$ with p-xylene or mesitylene affords (IX),[274] the structure of which was determined through an X-ray crystallographic study.[46]

A number of groups have studied $R_nM\cdot base_m$ complexes. Reaction of tribenzylboron and WCl_6 affords unstable Cl_5WCH_2Ph, which adds dipy to produce $Cl_5WCH_2Ph\cdot dipy$.[275] Reaction of $WCl_4\cdot 2THF$ with dibenzylmagnesium yields diamagnetic red-brown $W(CH_2Ph)_4$, characterized through use of IR and proton NMR spectra. Thermal decomposition of the species, which also adds dipy to afford $W(CH_2Ph)_4\cdot dipy$ has been studied.[275] Reaction of $MoCl_3(THF)_3$ with $[Li(CH_2)_2PMe_2]_x$, or of $Li_4Mo_2Me_8$ with $Me_4P^+Cl^-$ affords diamagnetic, orange-red $Mo_2^{II}[(CH_2)_2PMe_2]_4$, in which bonding probably is best represented by (CXII) or (CXIII). The ^1H and ^{31}P NMR, IR and mass spectra of the product have been reported.[276]



(CXII)



(CXIII)

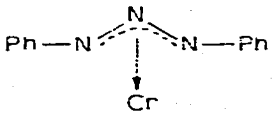
Müller and Holzinger have reported synthesis of unusually-stable brown-red, hydrolysis-resistant, pyrophoric, paramagnetic (2 unpaired electrons) tetraisopropylchromium through reaction of $CrCl_3$ with Pr^iMgBr. Unstable $Cr(Pr^i)_3$ is proposed as a reaction intermediate. Enhanced product yields under ultraviolet irradiation of reaction solutions suggest the intermediacy of free radicals.[277] Reaction of WCl_6 with trimethylaluminum in petroleum ether at -70° affords the explosive[278] WMe_6.[279]

The stabilization of alkyl complexes containing bases has been a subject of interest. Phenyldiphenyltriazenechromium(III) complexes, $Ph_2Cr(N_3Ph_2)\cdot 2THF$, $PhCr(N_3Ph_2)_2\cdot THF$, as well as $Cr(N_3Ph_2)_3$ and the adduct $Ph_2Cr(N_3Ph_2)\cdot(dipy)$ have been prepared. The title complexes were prepared through reaction of triphenylchromium and *N*-HN_3Ph_2, with elimination of benzene. The thermal and hydrolytic stability of the red-brown, paramagnetic complexes is strongly enhanced by the presence of the diphenyltriazene ligands, which probably function as chelating ligands, as shown in (CXIV).[280]

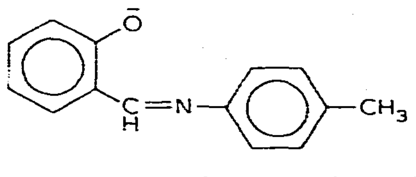
Diarylchromium(II) phosphine complexes have been studied by Seidel and Stoll. These complexes, $Cr(R)_2\cdot 2PR_3$ were obtained through reaction of $(2,4,6\text{-}Me_3C_6H_2)_2Cr\cdot(THF)_3$ and PR_3 in THF ($PR_3 = PEt_3$, PEt_2Ph) ($Cr(2,4,6\text{-}Me_3C_6H_2)_2\cdot 2PR_3\cdot 3THF$), through reaction of $Li_2CrPh_4\cdot 4THF$, PEt_3 and HCl in hexane ($CrPh_2\cdot 2PEt_3$), or through reaction of $CrCl_2$, PEt_3 and $CH_3C_6H_4Li$ in hexane/ether ($Cr(2\text{-}MeC_6H_4)_2\cdot 2PEt_3$). The brown-to golden-yellow, paramagnetic (4 unpaired electrons) species are formulated as *trans* planar monomeric complexes.[281]

New alkylchromium complexes have been prepared at below -30° through base-exchange reactions of $RCrCl_2(THF)_3$.[282] The new species have the general formula $RCrCl_2(base)_n$ (R = Me, Et): (n = 2, base = 2-methylpyridine, R = Me; n = 3, base = 3-Mepy, 4-Mepy, R = Me, Et; n = 4, base = H_2NPr^i, R = Me). Base-exchange reactions were also carried out with $H_2NC_6H_{11}$, piperidine, PEt_3 and $PBu^n{}_3$, but these led to the formation of ill-defined products and/or Cr-R bond-cleavage. Thermolysis data were taken to determine the relative stabilities of these complexes, and the electronic and steric basis of the observed stabilities was discussed.[282]

Complexes of the type $R_fCr(\text{bidentate Schiff base})_2 \cdot py$ or $R_fCr(\text{tetradentate Schiff base}) \cdot py$ ($R = Me_f$, Et_f, $Pr^n{}_f$; bidentate Schiff base = sal-N-p-tol (CXV), sal-N-$\underline{n}$-C_4H_9, sal, acac; tetradentate Schiff base = salen (CXVI) sal-phen, acen, bzac) exhibiting appreciable solid-state and solution stability have been synthesized through reaction of $R_fCrCl_2(NCCH_3)_3$ with the Schiff base, followed by crystallization from ethanol/pyridine. The electronic spectra and detailed magnetic susceptibility data are given. The temperature-dependence of the latter may be interpreted in terms of a weak antiferromagnetic exchange for a weakly-coupled linear chain model, or, for monomeric species, in terms of an in-plane chelate ligand and strong R_f-Cr out-of-plane bonding. Values of 10 Dq were determined from electronic spectra.[283]

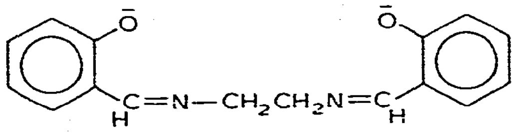


(CXIV)



N-*p*-tolylsalicylaldiminato(1-)
(sal-N-*p*-tol)

(CXV)



N,N'-ethylenebis(salicylaldiminato)(2-)
(salen)

(CXVI)

<u>Metal-metal bonded complexes</u>. Many of the metal-metal-bonded species reported this year have been discussed in the Sections on "simple" substitution products and complexes containing (η-Cp) or other ring systems. Several references have discussed modified procedures of synthesis of known metal-metal bonded species. Thus Ellis and Flom report the preparation of $M_2(CO)_{10}{}^{2-}$ ions (M = Cr, Mo, W) through reduction of the hexcarbonyls with Na/K

in THF.[181] It has been reported that these anions can also be prepared through use of C_8K/THF or, for M = Cr, electrochemically (Hg electrode in DMF).[284] For the latter a proposed mechanism envisions the electrochemical formation of $Cr(CO)_5^{2-}$ which then reacts with $Cr(CO)_6$ and H_2O to afford, ultimately, the observed products. Reaction stoichiometry is,[285]

$$4Cr(CO)_6 + H_2O + 4e^- \rightarrow Cr_2(CO)_{10}^{2-} + HCr_2(CO)_{10}^- + 4CO + OH^- \quad (15)$$

Reaction of $Mo(CO)_6$ with SiI_4, or of $W(CO)_6$ with HgI_2 or Hg_2I_2 affords $[(OC)_4MI]_2$ (M = Mo, W), characterized by infrared and mass spectra, and magnetic susceptibility measurements (diamagnetic).[61] For M = Mo, the structure of the complex, containing I bridges and a metal-metal bond, has been given.[61]

Flash photolysis of $(OC)_5M'-M(CO)_3(\eta-Cp)$ (M = Mo, W; M' = Mn, Re) affords $M'_2(CO)_{10}$ and $[(\eta-Cp)M(CO)_3]_2$. In CCl_4 the products obtained are $M'(CO)_5Cl$ and $(\eta-Cp)M(CO)_3Cl$. The electronic spectra are interpreted in terms of an accessible σ^* orbital with respect to the M'-M bond; thus the observed homolytic cleavage. Quantum yields were given.[286]

Nitrosyl complexes. Complexes containing the nitrosyl ligand continue to merit interest. Isaacs and Graham have investigated reactions of $Et_4N^+[R_3M'M(CO)_5^-]$ complexes (M = Mo, R_3M' = Ph_3Ge, Me_3Sn, Ph_3Sn, Ph_3Pb; M = W, R_3M' = Ph_3Si, Ph_2MeSi, Ph_3Ge, Ph_3Sn, Me_3Sn, Ph_3Pb) with $NO^+PF_6^-$ to afford yellow-to-orange trans-$R_3M'M(CO)_4NO$ products. Reactions of $X_3SnW(CO)_5$ (X = Cl, Br) with NO^+ in CH_2Cl_2 afford $XW(CO)_4NO$ species. The complexes were characterized by infrared and mass spectra, and bonding trends in the isoelectronic series, $Me_3SnW(CO)_5^-$, $Me_3SnW(CO)_4NO$, $Me_3SnRe(CO)_5$ were discussed.[286] Legzdins and Malito have studied the utility of NOCl as a nitrosylating agent. Reaction of NOCl with the $(\eta-Cp)M(CO)_3^-$ anions (M = Cr, Mo, W), and with $W(CO)_5Cl^-$ result in replacement of one carbonyl and the formation of neutral products, $(\eta-Cp)M(CO)_2(NO)$, green to gold, and $W(CO)_4(NO)(Cl)$.[287] Reactions of the neutral $(\eta-Cp)M(CO)_2(NO)$ with NOCl afford the non-carbonyl-containing $(\eta-Cp)M(NO)_2(Cl)$ (M = Cr, Mo, W). The identity of the products was confirmed by elemental analysis, and infrared and mass spectral measurements.[287] $(\eta-Cp)M(CO)_2(NO)$ reacts at -78° with $NOPF_6$ to give the green, reactive $[(\eta-Cp)M(CO)(NO)_2^+]PF_6^-$ products, which react with Lewis bases, L (= PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$) to give green

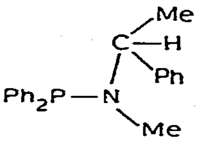
$[(\eta\text{-Cp})M(NO)_2L^+]PF_6^-$ products, and with halides (X^- = Cl^-, Br^-, I^-) to give the neutral $(\eta\text{-Cp})M(NO)_2X$ products.[288] $(\eta\text{-Cp})Mo(CO)_2(NO)$ fails to react with PF_3 or $SnCl_3^-$ under ultraviolet irradiation.[289] Reaction of $W(CO)_6$ with NOCl affords the polymeric $[W(NO)_2Cl_2]_n$, which reacts with Lewis bases to afford $W(NO)_2Cl_2L_2$ (L = PPh_3, $P(OPh)_3$).[290] Reaction of $(\eta\text{-Cp})Mo(CO)_2(NO)$ with (CXVII, (L)) affords the diastereoisomeric pair, $(\eta\text{-Cp})Mo(CO)(NO)(L)$ in about equal amounts, which was separated by preparative liquid chromatography or several fractional crystallizations. The coordinated aminophosphine, L, in these complexes can be transformed into the corresponding methoxyphosphine through successive reactions with HCl and CH_3OH.[291]

$(\eta\text{-Cp})M(NO)_2Cl$ (M = Cr, Mo, W) can be alkylated by R_3Al or R_2AlH in benzene to afford the green $(\eta\text{-Cp})M(NO)_2R$ (M = Cr, Mo, W; R = Ph, Me, Et, Bu^t), characterized by infrared, proton NMR and mass spectra. The dimeric $[(\eta\text{-Cp})Cr(NO)_2]_2$ can be conveniently prepared through zinc amalgam reduction of $(\eta\text{-Cp})Cr(NO)_2Cl$ in THF.[292]

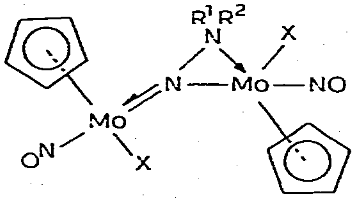
Hoch, Sasse and Ziegler have reduced $(\eta\text{-Cp})Cr(NO)_2Cl$ employing $NaBH_4$ in methanol/benzene, and have obtained ruby red, $[(\eta\text{-Cp})Cr(NO)(NH_2)]_2$, containing amido bridges. The same reaction carried out in the presence of water affords the di-μ-hydroxo complex, $[(\eta\text{-Cp})Cr(NO)(OH)]_2 \cdot 2H_2O$, which loses water in a stepwise fashion when heated under vacuum. The complexes have been characterized employing IR, proton NMR and mass spectral data.[293]

McCleverty and coworkers have prepared $[(\eta\text{-Cp})Mo(NO)(X)(I)]_2$ through reaction of $(Cp)_2Mo(NO)I$ with HX (X = Cl, Br, I, SMe, $SCMe_3$, SPh); cyclopentadiene was an additional product. Reaction of $(Cp)_2Mo(NO)I$ with RCO_2H (R = H, Me, Et) affords $(\eta\text{-Cp})Mo(NO)(O_2CR)(I)$. The results indicate that the substrate in solution is, in fact $(\sigma\text{-Cp})(\eta\text{-Cp})Mo(NO)(I)$. Reaction of $Cp_2Mo(NO)I$ and $[(\eta\text{-Cp})Mo(NO)X_2]_2$ (X = Br, I) with $PhNHNH_2$ and R_2NNH_2 (R = Me, Et) afford a variety of mono- and dinuclear products, containing halide and/or hydrazide bridges.[294] The products of certain of these reactions have been further studied. The reaction of $[(\eta\text{-Cp})Mo(NO)X_2]_2$ (X = Cl, Br, I) with $R^1R^2NNH_2$ ($R^1 = R^2$ = Me, Et; R^1 = Me, R^2 = Ph) afforded products formulated as (CXVIII) on the basis of an X-ray structural determination (AS, Structure of Organo-Transition Metal Complexes 1974/89).[295] $(\eta\text{-Cp})_2Mo(NO)I$ reacted with Me_2NNH_2 to afford first the complex containing a σ-bonded hydrazide, $(\eta\text{-Cp})Mo(NO)(I)NHNMe_2$, which upon heating in $CHCl_3$ also afforded (CXVIII). $[(\eta\text{-Cp})Mo(NO)I_2]_2$ reacted with

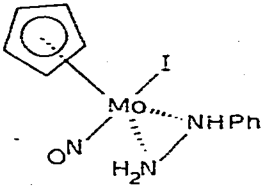
$PhNHNH_2$ to afford the Lewis base adduct $(\eta\text{-}Cp)Mo(NO)(I)_2(NH_2NHPh)$, which further produced a complex formulated as $[(\eta\text{-}Cp)Mo(NO)(I)\text{-}(N_2HPh)]_2$, containing terminal iodides and hydrazide bridges.[295] The complex analogous to (CXVIII) with R^1 = H, R^2 = Ph can be protonated with HBF_4/CH_2Cl_2 to yield a complex (CXIX), as determined through an X-ray investigation.[296] These results led to



(CXVII)



(CXVIII)



(CXIX)

a detailed Fourier-transform proton NMR study of the non-protonated precursor, and its reformulation as polymeric, $[(\eta\text{-}Cp)Mo(NO)(I)\text{-}(NHNHPh)]_n$.[296]

An ESR study of $Cr(CN)_5NO^{3-}$ in mixed water-glycol and water-glycerine solutions has been reported.[297]

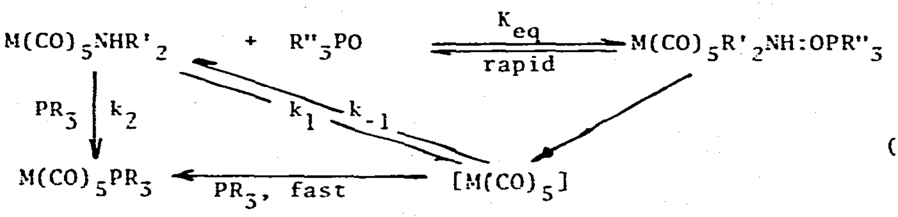
Kinetic and Mechanistic Studies

Black and Braterman have cited evidence against the existence of a trigonal bipyramidal $Cr(CO)_5$ fragment formed from the hexacarbonyl, as reported by Kundig and Ozin. The available data support the greater stability of a square-pyramidal fragment.[298]

Both Ewen and Darensbourg[299] and Nasielski, Vermeulen and Leempoel[300] have considered anomalies observed in rates of reaction of primary and/or secondary amine-containing-Group VI-B metal pentacarbonyls; *e. g.*,

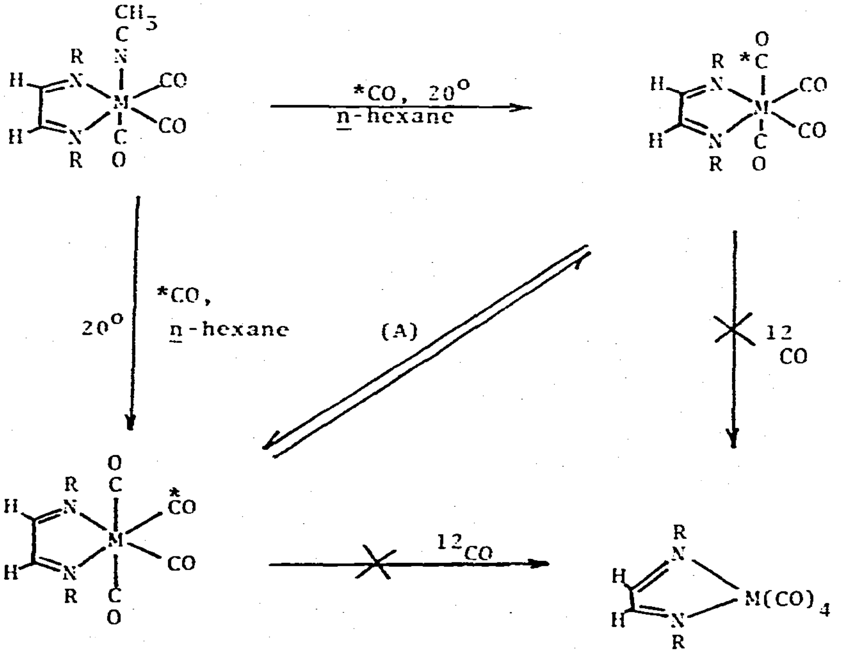
$$(amine)M(CO)_5 + PPh_3 \longrightarrow Ph_3PM(CO)_5 + amine \qquad (16)$$

The latter workers have implicated triphenylphosphine oxide as a cause of irreproducible results for (16); the former have presented spectroscopic evidence for the formation of hydrogen-bonded $R_3PO\cdot\cdot HNR_2M(CO)_5$ species and have presented strong evidence for the operation of mechanism (17) in reactions (16) containing primary or secondary amines:



(17)

Majunke, Leibfritz, Mack and tom Dieck have studied the incorporation of ^{13}CO into glyoxalbis(arylimine)tetracarbonylmetal complexes. Scheme (18) outlines the observed interconversions, Studies of the axial-equatorial ^{13}CO exchange were carried out employing ^{13}C NMR spectroscopy at -50° to 30°. It is proposed that the intramolecular process 18-A takes place from distorted octahedral ground states of the substrates through a trigonal prismatic transition state.[301]



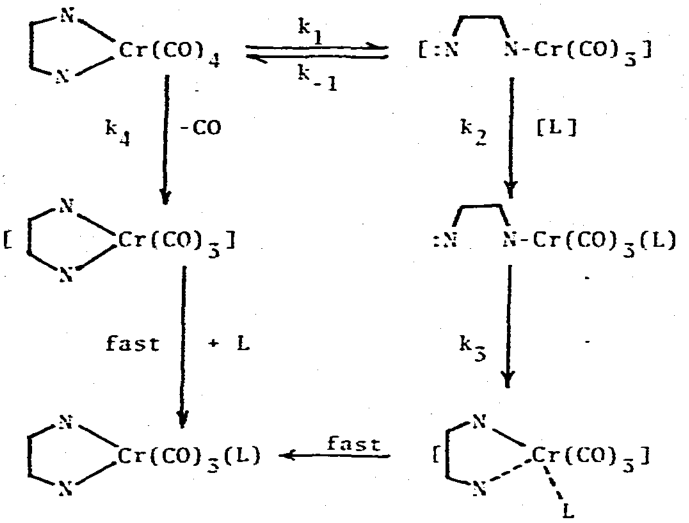
(18)

(M = Mo, R = Bu^t, p-tolyl, o-tolyl, 2,6-dimethylphenyl, 2,4,6-triisopropylphenyl; M = Cr, W: R = 2,6-dimethylphenyl)

McKerley, Faber and Dobson, in a reinvestigation of the kinetics and mechanism of (19) have presented evidence that the data are best encompassed within overall mechanism (20).[302]

$$L + (dipy)Cr(CO)_4 \rightarrow fac\text{-}(dipy)(L)Cr(CO)_3 + CO \qquad (19)$$

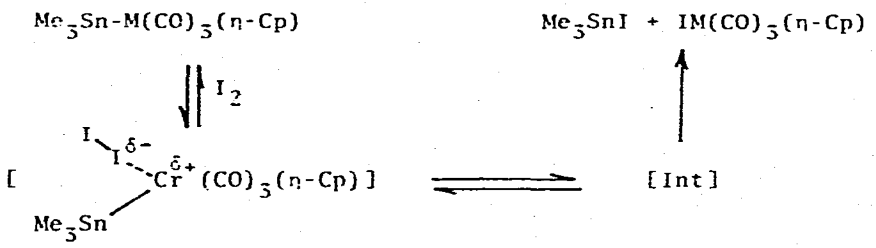
$(L = P(OCH_2)_3CCH_3,\ P(OEt)_3)$



(20)

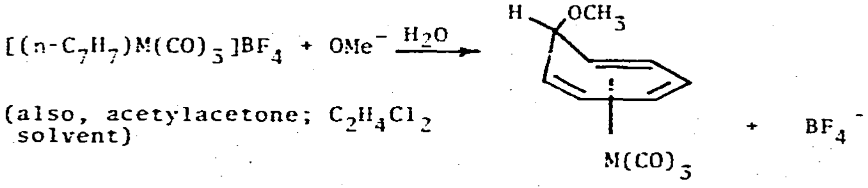
Connor and coworkers have studied the kinetics and mechanism of ring-closure in (bidentate ligand)$M(CO)_5$ complexes to afford (chelate)$M(CO)_4$ species.[106,107] For $(R_2PC_2H_4PR_2)M(CO)_5$ substrates (R = _cyclo_-C_6H_{11}, Ph, Me; M = Cr, Mo, W), activation parameters for ring-closure to afford $(R_2PC_2H_4PR_2)M(CO)_4$, together with observed steric acceleration in the series of bidentate ligands both support a predominantly dissociative mechanism for ring-closure.[107] In contrast the analogous studies of ring-closure in $(RSC_2H_4SR)M(CO)_5$ (R = _p_-XC_6H_4; X = H, Me, OMe, NMe_2, Bu^t; M = Cr, Mo) support a significant associative contribution to the process. Thus it was observed that the rate of ring-closure increased with increased electron-donation by X, but decreased with greater steric demands imposed by the bidentate ligand.[106]

Chipperfield, Ford, Hayter and Webster[303,304] have completed kinetics investigations of the cleavage of Sn-M bonds in Me_3Sn-$M(CO)_3$(η-Cp) (M = Cr, Mo, W), to afford Me_3SnI and $IM(CO)_3$(η-Cp) (carbon tetrachloride solution). Results indicate the reactions to proceed _via_ initial formation of a charge-transfer complex and an intermediate before product formation (21); the process thus is evisioned as an electrophilic cleavage of the metal-metal bond. Spectrophotometric evidence for the formation of the intermediate was obtained for M = Cr.[304]



(21)

The mechanism of nucleophilic addition to tricarbonyl(η-tropylium) cations of the Group VI-B metals e. g., (22) has been studied by Al-Kathumi and Kane-Maguire.[305] The reactions obey second-order kinetics, and the insensitivity of rate to the identity of the metal (Cr, Mo or W) suggests ring-attack, although addition of MeO⁻ to a carbonyl carbon in the initial step cannot be ruled out. The data are inconsistent with the conclusion of Hackett and Jaouen[269] that the tropylium ring is more electrophilic in the Cr complex than for Mo. Their results may alternately be interpreted as reflecting the greater susceptibility of attack at Mo than at Cr.[305]



(22)

Kleinberg and co-workers studied the kinetics of (23) employing NMR spectroscopy and have found the reaction to be first-order in $(\eta\text{-Cp})_2WH_2$, although the order with respect to $PhCCl_3$ could not be determined. A free-radical chain mechanism was implicated. It was also found that when 3,4-dichlorobenzotrichloride was employed, the rate was accelerated appreciably.[306]

$$(\eta\text{-Cp})_2WH_2 + 2\ PhCCl_3 \xrightarrow{\text{glyme}} (\eta\text{-Cp})_2WCl_2 + 2\ PhCHCl_2 \qquad (23)$$

The kinetics of the thermal decomposition of $Cr(CO)_6$[307] and of various $(\eta\text{-arene})_2Cr$ complexes,[308] and of the reaction of O_2 with the latter (M = Cr, Mo)[309] have been studied by Soviet workers. Decomposition of $Cr(CO)_6$ at temperatures from 125° - 445° proceeds *via* four steps, for two of which activation energies have been determined.[307] The thermal decomposition of $(\eta\text{-}C_6H_6)_2Cr$, $(\eta\text{-}C_6H_6)(\eta\text{-}EtC_6H_5)Cr$, $(\eta\text{-}EtC_6H_5)_2Cr$ and $(\eta\text{-}EtC_6H_5)(\eta\text{-}Et_2C_6H_4)Cr$ has been studied by both statistical and flow methods, which give results in good agreement. The decomposition is preceeded by adsorption of the substrates on the reaction surface.[308] Reaction of oxygen with $(\eta\text{-}C_6H_6)_2Cr$, $(\eta\text{-}EtC_6H_5)_2Cr$, $(\eta\text{-cumene})_2Cr$, $(\eta\text{-}p\text{-xylene})_2Cr$, $(\eta\text{-}EtC_6H_5)(\eta\text{-}Et_2C_6H_4)Cr$, $(\eta\text{-}EtC_6H_5)(\eta\text{-}Et_2C_6H_4)Mo$, $(\eta\text{-}Et_2C_6H_4)_2Mo$ and $(\eta\text{-}EtC_6H_5)_2Mo$ proceeds _via_ a second-order rate law. Activation parameters have been determined, and rates interpreted in terms of the effective electronegativities of the metal atoms.[309]

Nohr and Espenson have studied the acidolysis and oxidative cleavage of benzylchromium^{2+} cations in aqueous perchloric acid, which proceed according to (24)

$$[(H_2O)_5CrCH_2Ph]^{2+} \xrightarrow[HClO_4]{aq.} Cr(H_2O)_6{}^{3+} + C_6H_5CH_3 \qquad (24)$$

Oxidizing agents employed included Fe^{3+}, Cu^{2+}, $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, O_2 and H_2O_2.[310] The first-order results were interpreted in terms of unimolecular homolysis of the Cr-C bond followed by rapid oxidation.

Catalysis and Polymerization

Again this year there has been great interest in the use of Group VI-B metal carbonyls and derivatives in catalytic systems which promote olefin metathesis, (_e. g._, Eq. 25). Both Agapiou and McNelis[311] and Krausz, Garnier and Dubois[312] independently

$$R\text{-}CH{=}CHR' \rightarrow RCH{=}CHR + R'CH{=}CHR' \qquad (25)$$

reported that photolysis of $W(CO)_6$ in CCl_4 affords an olefin metathesis catalyst which does not require a co-catalyst. The first-named workers also found that $(\eta\text{-mesitylene})W(CO)_3$ and $(CH_3CN)W(CO)_5$ were active to a lesser extent.[311] Krausz and coworkers presumed $W(CO)_5Cl$ to be the active catalytic agent,[312] but Agapiou and McNelis, through independent synthesis and infrared spectra of reaction solutions, showed $W(CO)_4Cl_2$ to be present in the catalytic solutions.[313]

Metal carbonyl solutions containing co-catalysts have also been subject of attention as catalysts for olefin metathesis. $W(CO)_5NCCH_3/EtAlCl_2$, $W(CO)_5NCCH_3/AlCl_3$ in benzene-hexane, and

$W(CO)_6/EtAlCl_2$ under ultraviolet irradiation have been found to be active metathesis catalysts. An unstable $W(CO)_5$ species was proposed to be the active species.[314] The systems $W(CO)_5L/EtAlCl_2/O_2$ and $W(CO)_5L/AlCl_3$ (L = CO, PPh_3, $P(\underline{n}\text{-}Bu)_3$, $P(OPh)_3$) also exhibit olefin metathetical catalytic activity. Infrared evidence indicates that activation of the metal carbonyl occurs through interaction of the Al-containing co-catalysts with the carbonyl oxygen *trans* to L.[315]

Mortreux and Blanchard have found that phenol and resorcinol function as co-catalysts to $Mo(CO)_6$ in the metathesis of disubstituted alkynes.[316] This observation points to the importance of the -OH function in the activation of the catalyst in heterogeneous catalysis. Heterogeneous catalytic systems containing $Mo(CO)_6$ have been studied in detail by Burwell and Brenner.[317,318] $Mo(CO)_6$ adsorbed on γ-Al_2O_3 affords metal carbonyl fragments attached to the support, probably by -OH-metal interactions. Evidence indicates that species of the types (support)-$Mo(CO)_5$, (support)-$Mo(CO)_4$ and (support)-$Mo(CO)_3$ are present.[317] The catalytic activity of the latter in the metathesis of propylene has been demonstrated.[318] At high temperatures, addition of O_2 affords (support)-$Mo(CO)_2(O_2)$ and (support)-Mo^{II} species, which exhibit substantial catalytic activity. In the latter heterogeneous catalytic system, it is likely that support oxygen is coordinated to molybdenum.[318]

In contrast to some of the preceding results, which seemingly indicate several possible catalytic species to be active in olefin metathesis, Basset, Bihou, Mutin and Theolier have studied homogeneous olefin metathesis catalysts of tungsten in which the metal complex exhibits a variety of degrees of substitution, types of substituents, stereochemical arrangements and oxidation states, and for which various cocatalysts are employed. For all homogeneous systems, catalytic results (*cis*-2-pentene catalysis; ratios of *trans*- to *cis*-butenes and -hexenes) were similar, seemingly implicating the same catalytic species in each catalytic system. In contrast, heterogenous catalytic systems employing a γ-Al_2O_3 support give different results; thus the surface imposes an influence on the steric course of methathesis.[319]

Howe studied the ESR spectra of various heterogeneous catalytic systems (silica support), $Mo_2(CH_3CO_2)_4$, $M_2(CH_2SiMe_3)_6$ (M = Mo, W), $W(CO)_6$, WMe_6, $Cr(CO)_6$ and $Cr(CH_2CMe_3)_4$, at elevated temperatures.[320] For the Mo systems, signals attributable to square pyramidal Mo^V (and to O_2^- derived from interaction of O_2

with tetrahedral Mo^{V}) were observed. These results support a common active site, but one of undetermined nature, in the catalysts themselves. For W, the metal atom in the active catalyst probably has the same oxidation state as it does in the Mo catalysts. Spectra observed for the Cr systems closely resemble those for supported Cr catalysts obtained through the reduction of Cr_2O_3, or impregnation of silica with Cr^{II} or Cr^{III} solutions.[320] The kinetics for disproportionation of propylene over $(\eta\text{-}C_3H_5)_4Mo/\text{-}SiO_2$ indicated that coordinatively-unsaturated Mo^{4+} ions were the active centers.[321,322]

$PhWCl_3$ has also been found to be an active olefin metathesis catalyst.[323] Addition of $AlCl_3$ increases the activity, while CO increases the activity still further. Among tungsten carbonyl species found in the presence of CO, $W(CO)_6$ was identified in the reaction solution.

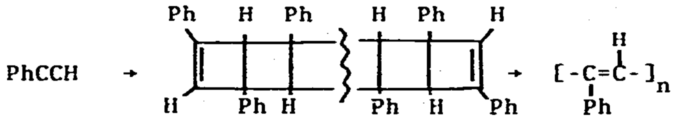
Wolovsky and Nir have demonstrated that the $WCl_6/EtAlCl_2$ catalytic system for olefin metathesis is a true homogeneous system.[324] Menapace and coworkers have found that the metathesis of 2-pentenes is sensitive to the order in which the components of $WCl_6/Et_3Al_2Cl_3/PhNH_2$ were added. At Al/W ratios > 3, dimerization, rather than metathesis, is the dominant process for terminal olefins (propylene). For 2-pentenes, no dimerization is observed at high Al/W ratios, suggesting the catalyst to allow coordination of terminal but not internal olefins in the dimerization process. A possible mechanism is presented.[325]

The metathesis of 2-pentene employing $MoCl_2(NO)_2$, $MoCl_2\text{-}(NCEt)_2$ and $MoCl_2(NO)_2(OPPh_3)_2$ with varying ratios of the cocatalysts $EtAlCl_2$, $LiBu^n$ or $AlBr_3$ has been studied by Taube and Seyferth,[326] who have also probed the nature of the catalytic solutions through studies of the $\nu(NO)$ region of the IR spectra (1400-2000 cm^{-1}).

Studies of the polymerization of olefins employing Group VI-B organometallic catalysts have been of continuing interest. Among the catalytic systems studied have been methyl methacrylate/-$(\eta\text{-allyl})_3Mo$ + pyridine, which probably functions by an anionic mechanism,[327] and ethylene/$(\eta\text{-allyl})_3Cr$ + source of active hydrogen, e. g., organic acids, alcohols or water.[328] A number of investigations employing η-allyl-Group VI-B metal catalysts on various support materials in heterogeneous catalysis have also been reported. Ermakov and coworkers have found that butadiene polymerization by $(\eta\text{-allyl})_2Cr$ depends upon the nature of the catalyst support.[329] Karol and Johnson have prepared catalysts for the polymerization of ethylene through deposition of chromocene, (η-benzene)$_2$Cr, (η-cumene)$_2$Cr, (η-allyl)$_2$Cr or (η-allyl)$_3$Cr on high surface area silica-alumina or silica supports. Here too, catalytic activity was found to vary with the nature of the support; for (η-cumene)$_2$Cr, differences in catalytic activity were also noted upon addition of cyclopentadiene. The observed order of activity was chromocene/silica > chromocene/silica-alumina > (η-arene)$_2$Cr/silica-alumina > (η-allyl)$_n$Cr/silica.[330] Interaction of (η-allyl)$_3$Cr with the OH groups of silica gel leads to the evolution of propylene, and the formation of an active polymerization catalyst for ethylene.[331] The nature of such catalysis has also been studied. Demin and coworkers have also determined that such processes are first order with respect to monomer, and have calculated an activation energy of 5 ± 1 kcal/mole and other characteristics of the reaction employing radioactive quenching techniques.[332] Tris(η-allyl)Cr and bis-(η-allyl)(butoxy)Cr on silica/alumina promote the homo- and copolymerization of butadiene and isoprene; the stereospecificity and reactivity ratios were the same for both catalysts, and for Cr_2O_3. A living chain mechanism was envisioned for the process, and the nature of the species involved was discussed.[333] Very similar results were also discussed by the same group in another report.[334] (η-Cp)$_2$Cr supported by silica or SiO_2/Al_2O_3 has been employed as a catalyst for the polymerization of ethylene, and the conditions under which polymers of various molecular weights could be prepared employing this catalytic system were studied.[335]

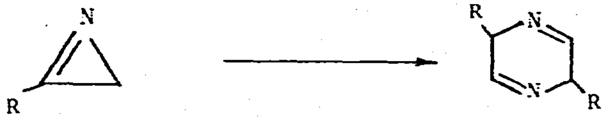
(η-Allyl)$_4$Mo/silica catalysts have been found to exhibit differing catalytic behavior, depending upon the oxidation or reduction of the silica. The reduced catalyst, which contains Mo^{2+}, is an extremely active catalyst for the hydrogenation of ethylene, while the oxidized catalyst, containing Mo^{4+} surface species is active in the catalytic oxidation of hydrogen at temperatures as low as 100° C.[336] Pt-Mo and Pd-Mo heterogeneous catalysts, prepared through deposition of η-allyl complexes of Mo, Pd and Pt on silica support have also been reported;[337] a Japanese patent describes the preparation of Cr_2(η-allyl)$_4$, an olefin polymerization catalyst.[338] The observed thermal desorption of CH_2=CHMe from Cr_2O_3 or MoO_3/AlO_3 and by (η-allyl)$_4$Mo from silica were taken to indicate that symmetrical η-allyl and asymmetrical σ-allyl complexes were intermediates in the metal oxide catalysis of CH_2=CHMe to CH_2=CHCHO.[339]

The use of $(\eta\text{-arene})Cr(CO)_3$ complexes as catalysts in the selective hydrogenation of olefins, including vegetable oils,[340] has received attention. Cais and coworkers have found that $(\eta\text{-arene})Cr(CO)_3$ complexes of condensed aromatics such as phenanthrene, naphthalene and anthracene are considerably more active in this regard than are analogous species containing simple arenes. The enhanced catalytic activity is explained in terms of two relatively long Cr-C bonds, more easily broken, for such species. Coordinating solvents such as THF and acetone accelerate the rates of hydrogenation. For acetonitrile, it was shown that $(CH_3CN)_3Cr(CO)_3$ was produced, and was the active catalytic agent.[341] The most efficient catalytic system for the hydrogenation of methyl sorbate was found to be $(\eta\text{-naphthalene})Cr(CO)_3/CH_3CN$.[342] Hydroxylation of benzene, naphthalene and 2-methylnaphthalene by oxygen in the presence of $Mo(CO)_6$ in CH_3CN solution is reported to proceed _via_ formation of $(\eta\text{-arene})Mo(CO)_3$ intermediates.[343] $(\eta\text{-Arene})Mo(CO)_3$ species, generated _in situ_ from $Mo(CO)_6$ and arenes such as PhMe and PhOMe have been employed in a variety of Friedel-Crafts-type reactions, including alkylations, arylations and sulfonylations.[344-346] They are generally more selective than conventional Friedel-Crafts catalysts, affording principally the _para_ isomers when an aromatic species is the substrate. Poly(_p_-phenylene) has also been synthesized employing $(\eta\text{-arene})Cr(CO)_3$ complexes to improve solubility during polymer formation _via_ Diels-Alder reactions.[347] The polymerization of terminal and internal acetylenes[348] to linear polyconjugated compounds has also been effected employing $(\eta\text{-arene})M(CO)_3$ (M = Cr, Mo, W) species. The mechanism is proposed to involve a series of successive [2 + 2] cycloadditions to afford "ladder-type" intermediate species, which afford chains through olefin metathesis and isomerization (26).[348]



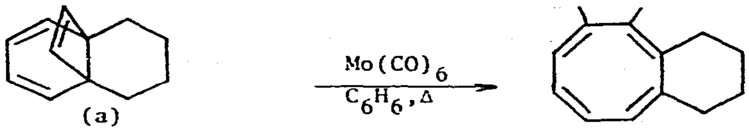
(26)

Other examples in which the hexacarbonyls themselves afford catalysis have been reported. Azirines have been dimerized in the presence of $Mo(CO)_6$ in THF at room temperature over 24 hours; $Cr(CO)_6$ and $W(CO)_6$ are also effective over longer reaction times. The dimerization products contain pyrazine bridges, _e. g._, (27),



(27)

A mechanism involving initial formation of a $[M(CO)_5]$ intermediate was proposed.[349] Rearrangement of (28-a),



(and bond-shift isomer)

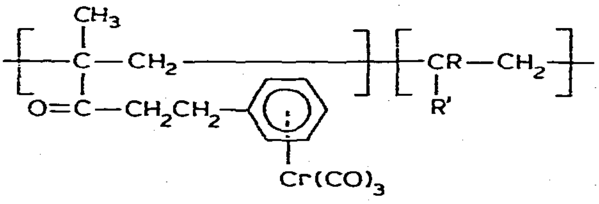
(28)

has also been observed in the presence of $Mo(CO)_6$. A possible mechanism which involves [1,5] sigmatropic migration within the metal coordination sphere is discussed.[350] Olefins ((-)-limonene, p-menth-1-ene) undergo stereospecific epoxidation with t-pentyl hydroperoxide in the presence of $Mo(CO)_6$; mechanistic implications, which propose Mo carbonyl intermediates containing coordinated olefin and hydroperoxide, are discussed.[351] The preparation of epichlorohydrin through epoxidation of CH_2=$CHCH_2Cl$ by PhCHMeOOH or MeCOOH (peroxides) in the presence of $Mo(CO)_6$, $pyMo(CO)_5$ or $MoCl_5$ also has been reported.[352] Molybdenum naphthenate also catalyzes the continuous hydroperoxide epoxidation of olefins such as propylene, according to a Hungarian patent.[353]

Several other polymerization catalysts have been described in the patent literature. The catalysts and monomers reported include $(\eta\text{-}Cp)Cr(CO)_3H/SiO_2$ at 110°-900°, optional Et_3Al co-catalyst, ethylene and propylene;[354] $M(CO)_n(PR^1R^2R^3)_{6-n}$ (M = Mo,W; n = 3-5), organoaluminum compounds and halogenated carboxylic acids, alicyclic unsaturated monomers;[355] $(OC)_5W[C(OEt)Ph]/TiCl_4/h\nu$, cyclopentene;[356,357] $W(CO)_6$/gallium bromide, cycloalkadi- and -trienes. An easily handleable, thermally cross-linkable polybutadiene has also been prepared through polymerization of 1,3-butadiene and vinyltoluene employing a $(\eta\text{-allyl})(OC)_3(THF)$-(trifluoroacetate)Mo catalyst, and adding a peroxide prior to crosslinking.[358]

Highly stereoregular polymers were obtained through polymerization of 1,5-cyclooctadiene and cyclopentene through ring-opening employing WCl_6/ethyldiazoacetate. The possible mechanism of the catalytic effect was discussed.[359] $(\eta\text{-Allyl})_4Mo/SiO_2$ and that complex and other oxide carriers, (Al_2O_3, Cr_2O_3, Fe_2O_3,-Co_3O_4) were studied as catalytic systems for the synthesis of ammonia.[360] Carbon monoxide is reversibly absorbed on SiO_2-supported $Cr^{II}(NO)_2$ surfaces to afford $-Cr^{II}(NO)_2(CO)$. The adsorption was studied by infrared spectroscopy.[361]

Polymers in which a Group VI-B organometallic functionality is incorporated into the polymer chain have also received attention. Pittman and coworkers have continued their studies of polymers containing $-Cr(CO)_3$ bonded to arene groups contained in the polymer chains. They have described the polymerization of (η-benzyl acrylate)$Cr(CO)_3$ in detail, including a description of the application of the Strohmeier reactor to the polymerization.[362] (η-Benzyl acrylate)$Cr(CO)_3$ has also been incorporated into a variety of organic copolymers,[363] for example, into linseed oil films. The ultraviolet irradiation of such films produces materials which contain chromium oxide particles within the films. The copolymerization of organic monomers (acrylonitrile, styrene and methyl methacrylate) with (η-phenylethyl methacrylate)$Cr(CO)_3$ affords polymers of the type (CXX); the substrate can also be homopolymerized in ethyl acetate at 70°.[364] The $-Cr(CO)_3$ moiety can also be incorporated into siloxane polymers such as (CXXI) through reaction of the polymeric material with $Cr(CO)_6$ under various conditions. From 3 to 19 per cent of the arene rings were complexed in this manner.[365] Biedermann and Graf have studied the reactions of $M(CO)_6$ (M = Cr,[366] W[367]) with 4-pyridylethylene under forcing conditions, which have afforded polymeric products of the types $[M(4\text{-}C_7H_7N)_x(CO)_{6-x}]_n$ (M = Cr, x = 3-6; M = W, x = 2,4,5), characterized employing infrared spectra.



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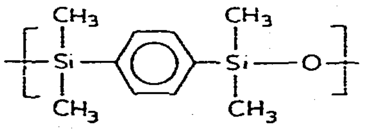


(CXXI)

Spectroscopic Studies

Photolysis studies, photoelectron spectra and molecular orbital studies. There has been continued interest in the study of photochemical production of coordinatively-unsaturated fragments of the Group VI-B metal carbonyls, and their geometries and reactions. Perutz and Turner have studied the IR spectra of ^{13}CO-enriched $M(CO)_6$, and $M(CO)_5$ (M = Cr, Mo, W) produced by photolysis at 20° K in argon or methane matrices. The carbonyl stretching spectra observed for $M(CO)_6$ well-fit those expected on the basis of the Cotton-Kraihanzel energy-factored force field. For $M(CO)_5$, the spectra are consistent with a square-pyramidal (C_{4v}) fragment, and calculations based upon intensity measurements predict an axial-equatorial bond angle of 90-95° in these species. The carbonyl stretching spectra and force constants obtained are almost independent of the identity of the matrix material.[368] However, studies of the visible absorption spectra of $M(CO)_5$ in a variety of matrix materials (Ne, Xe, CH_4, SF_6, Ar, Kr, CF_4) demonstrate that that absorption is very sensitive to the identity of the matrix. The observation is interpreted in terms of a stereospecific interaction of the matrix with $M(CO)_5$, the shifts being attributable to the different strengths of interaction, and slightly differing bond angles in the metal carbonyl fragments. The results indicate that interpretation of the results of matrix-isolation and co-condensation experiments must be treated with caution, since observed spectra may result from a stereospecific interaction between fragment and matrix, rather than being indicative of the nature of an isolated sub-coordinate species.[369] Ultraviolet photolysis of $Cr(CO)_6$ in Ar matrices doped with CO has also provided evidence for the formation of weakly-interacting $Cr(CO)_5\cdot\cdot Ar$ and $Cr(CO)_5\cdot\cdot CO$; $Cr(CO)_4$ was also observed.[370] In concentrated matrices the formation of a $Cr(CO)_5\cdots X$ species, where X is a $Cr(CO)_x$ fragment, was inferred. The results indicate that reducing CO concentration and increasing Cr atom concentration in co-condensation experiments in an attempt to generate fragments of lower coordination number may instead increase the chance of the formation of polynuclear fragments.[370] It is also concluded that the presence of excess CO requires treatment of condensation experiment results in terms of mixed matrices, greatly complicating interpretation.[370]

Detailed photolysis studies of matrix-isolated $Mo(CO)_6$ have provided evidence for the formation of $Mo(CO)_4$ and $Mo(CO)_3$ fragments, as well as $Mo(CO)_5$. Carbon-13 monoxide enrichment studies provide evidence that the fragments are surprisingly asymmetric, and are little-changed in geometry from those expected to be produced upon ligand-removal. Thus Mo(CO)$_4$ exhibits C_{2v} symmetry, with angles of 174° and 107°, while Mo(CO)$_3$ is a trigonal pyramid (C_{3v}, with internal angles of about 105°). These geometries are consistent with those expected on the basis of theoretical predictions by Burdett,[371] and by Elian and Hoffmann.[383] Analogous results are indicated for Cr and W.[372]

Plane-polarized light has been used to produce oriented Cr(CO)$_5$ (C_{4v}) in a frozen methane matrix. The study has permitted the determination of the symmetry of the 489 nm transition in Cr(CO)$_5$ to be ($^1A_1 \rightarrow {}^1E$).[373] Similarly the symmetries of the MCO bending modes are A_1 (659 cm^{-1}) and E (647 cm^{-1}), consistent with results for Mn(CO)$_5$Br. Various possible product orientations which can result from decay from a trigonal bipyramidal (D_{3h}) excited state to the square-pyramidal (C_{4v}) ground state in the Cr(CO)$_5$ fragments produce apparent rotation of the fragment in the matrix upon irradiation with plane polarized light.[373]

Photolysis at 366 nm of W(CO)$_5$L (L = py, 3-Brpy) in an Ar matrix at 12° K affords W(CO)$_5$. The process is reversible (photochromic) upon irradiation at 435 nm. Evidence was also obtained for formation of free CO upon irradiation, and thus both loss of L and CO can occur upon photolysis of these substrates.[374]

The quantum yield for the photoproduction of Cr(CO)$_5$(py) in cyclohexane has been found to be 0.67 ± 0.02 for [Cr(CO)$_6$] = 3 x 10^{-4} M and [py] = 10^{-2} M, demonstrating the presence of a radiationless process in competition with photodissociation.[375] The value for the quantum yield (1) previously given for analogous systems[376] thus is in error.

Absorption and emission spectra for (L$_2$)M(CO)$_4$ complexes (M = Cr, Mo, W; L$_2$ = dipy, o-phen, 5-Me-phen, 5-Cl-phen, 5-Br-phen and 5-NO$_2$-phen) have been recorded and the data indicate that the lowest excited state for the substrates is charge-transfer in character. For M = Mo, W, emission was observed, with quantum yields of 0.02-0.07 at 77° K in ether/pentane/ethanol. The photosubstitution in cis-(py)$_2$W(CO)$_4$ with a variety of L (L = PPh$_3$, py, MeCN, t-4-styryl-py) was found to be efficient, but for the (L$_2$)M(CO)$_4$ complexes, quantum yields were significantly lower, showing that the lowest charge-transfer excited state is unreactive.[377]

The photochemistry of (η-arene)Cr(CO)$_3$ complexes has been studied by two groups. Nasielski and Denisoff have determined the quantum yield for the photolysis of (η-mesitylene)Cr(CO)$_3$, which afforded (η-mesitylene)Cr(CO)$_2$(L) (L = N-dodecylmaleimide) in benzene at 313 nm to be 0.90 ± 0.09. The yield may, in fact, be less than 1, indicating that a radiationless decay process may account for the possible deficit.[378] Wrighton and Haverty have determined the quantum efficiency for formation of (η-arene)-Cr(CO)$_2$(py) (arene = benzene, mesitylene) to be *ca*. 0.72 and to be independent of wavelength and pyridine concentration. (η-Arene)Cr(CO)$_3$ complexes quench triplet-excited benzil; the quantum efficiency of product formation is lower than for direct irradiation. The results are consistent with dissociative loss of CO as the primary excited-state decay process for the substrates, results which are in contrast to the corresponding thermal reactions of (η-arene)Cr(CO)$_3$, which proceed *via* loss of the arene, rather than CO.[379]

Flash photolysis of (OC)$_5$M'-M(CO)$_3$(η-Cp) in isooctane (M = Mo, W; M' = Mn, Re) affords M'$_2$(CO)$_{10}$ and [(η-Cp)M(CO)$_3$]$_2$ in high chemical yield.[380] This process is photolytically reversible in that photolysis of mixtures of the two products affords the mixed complexes.[381] In CCl$_4$ the photolysis products for all substrates are (η-Cp)M(CO)$_3$Cl and/or and M'(CO)$_5$Cl. Thus both forward and reverse processes involve homolytic metal-metal bond fission. The results indicate that for each system the photolysis populates a sigma orbital which is antibonding with respect to the metal-metal bond.[380,381] Another photolysis study, of [(η-Cp)Mo(CO)$_3$]$_2$ in cyclohexane, THF and acetonitrile, reveals the formation of two photolysis intermediates, which each regenerate the substrate, although at vastly differing rates. The evidence indicates the two to be (η-Cp)Mo(CO)$_3$, resulting from metal-metal bond homolysis, and (η-Cp)$_2$Mo$_2$(CO)$_5$, resulting from CO dissociation, which have a common photochemical origin.[382] In the presence of Br$^-$, photolysis of this dimer can afford, in addition to (η-Cp)Mo(CO)$_3$Br, (η-Cp)Mo(CO)$_3^-$ and (η-Cp)Mo(CO)$_2$X$_2^-$, depending upon the conditions employed.[383] The process is photochromic, at 30 per cent efficiency at 60°, but is less so in the presence of greater than stoichiometric amounts of Br$^-$.[383]

Elian and Hoffmann have employed extended Hückel calculations to study energy ordering, symmetry and the extent in space of M(CO)$_3$, M(CO)$_4$ and M(CO)$_5$ fragments and their abilities to interact with other ligands. Also discussed were the pyramidality of M(CO)$_5$, metal-metal bond formation, and other topics of interest to reactivity and stereochemistry in metal carbonyl complexes.[384] Rossi and Hoffmann have also employed a unified molecular orbital approach to studies of pentacoordinate metal carbonyls of C_{4v} and D_{3h} symmetry.[385] The Hartree-Fock-Slater method, employing a basis set of a complete double zeta set of STO's supplemented with two 4p sets on Cr have been used to calculate electronic charges on Cr, C and O for CO and $Cr(CO)_6$.[386] The electronic spectrum of $Cr(CO)_6$ has been reported, and the electronic structure of this species has been studied through SCF MO calculations employing the Roothaan scheme. Both zero differential overlap and CNDO approximations were employed, the first using the valence orbitals on Cr, the latter also employing orbitals on C and O. Observed transition energies were compared to those determined through the zero differential overlap method.[387]

The ultraviolet-visible spectra for $LW(CO)_5$ complexes (L = quinuclidine, cyclohexylamine, piperazine, piperadine and 1,4-diazobicyclo[2.2.2]octane) have been obtained, and interpreted on the basis of a simplified Gray-Beach (*AS* 1968/295) molecular orbital calculation.[388] Infrared, Raman and electronic spectra have also been obtained for $W_2(CO)_{10}^{2-}$ and $HW_2(CO)_{10}^{-}$. Electronic transitions and the W-W and W-H-W stretching modes have been assigned.[389] The electronic spectra for $MnCr(CO)_{10}^{-}$ and $Cr_2(CO)_{10}^{2-}$ have also been assigned as part of a study of $MM'(CO)_{10}^{-n}$ complexes (M = M' = Mn, Tc, Re; M = Mn, M' = Re, n = 0 were also discussed) on the basis of semi-empirical molecular orbital calculations.[390]

An extended Hückel molecular orbital analysis of reactivity for $(\eta\text{-Cp})_2M$, $(\eta\text{-Cp})_2M(CO)$ (M = Cr, Mo) and $(\eta\text{-Cp})_2W(CO)_2$ has been carried out. Correlation diagrams for formation of $(\eta\text{-Cp})_2MoH_2$ from $(\eta\text{-Cp})_2Mo$ and H_2, and for formation of $(\eta\text{-Cp})_2W(H)(Ph)$ by insertion into aromatic CH bonds have also been discussed. The dominant factors in reactivity (influences on energies of transition states) were adduced to be, (a) inter-electronic replusions associated with various metallic d-electron configurations, and, (b) steric encumbrance of coordination sites at the metal arising from the presence of the ring ligands. The stability of the 20 electron $(\eta\text{-Cp})_2W(CO)_2$ and of $(\eta\text{-Cp})W(H)(Ph)$ may be due to decreased repulsive interaction among ligands.[391] Molecular orbital results (SCCC) for a variety of isoelectronic metal tricarbonyls, including $(\eta\text{-}C_6H_6)Cr(CO)_3$ have also been discussed.[392]

Several studies involving photoelectron spectroscopy (PES) have appeared in the literature. Stelzer and Unger have employed ultraviolet PES to obtain the first vertical ionication potentials for a series of phosphine ligands (L) ($R_{3-n}PX_n$, R = Me, Bu^t; X = H, F, Cl; n = 0-3, and $(Me_3N)_{3-n}PX_n$; X = F, Cl; n = 0-2), and have proposed that these values afford a measure of the σ-donating abilities of L. The ligands then could be classified as to their π-bonding ability through comparison of ν(CO) and carbonyl stretching force constants for their cis-$L_2Mo(CO)_4$ complexes; ten new complexes of this type were also synthesized for the first time.[393] Grim and Matienzo have reported the photoelectron spectra for some fifty molybdenum carbonyl complexes. A plot of metal binding energy vs. calculated charge (for different oxidation states of Mo) indicates that an energy shift of 1 ev in the $Mo(3d_{5/2})$ binding energy corresponds to 0.3 + charge unit on Mo. The results also indicate ligands which are strong σ-donors and poor π-acceptors increase the charge on the metal, decreasing the metal binding energies.[394]

The ultraviolet PES of the series of complexes (η-Cp)-(η-C_7H_7)M (M = Zr, Nb, Mo) have been obtained. Both metal and ligand contribute significantly to MO's of δ symmetry; the only slight decrease in 4d ionization energy along the series may be contrasted to the observation for the analogous 3d series. This probably arises from smaller pairing energies in the 4d series.[395] Non-parameterized, Fenske-Hall type (AS, Mn, Tc, Re 1972/81) molecular orbital calculations and PES of open and closed-shell $(\eta\text{-}Cp)_2ML_2$ complexes, including $(\eta\text{-}Cp)_2MCl_2$ (M = Cr, Mo) and $(\eta\text{-}Cp)MoH_2$ have been reported. The MO calculations are consistent with the PES and also ESR results.[396] Green, Jackson and Higginson have reported PES for the eighteen-electron systems $(\eta\text{-}Cp)_2MR_2$ (M = Mo, W; R = H, Me) and $(\eta\text{-}Cp)_2ML$ (M = Mo, L = CO; M = Mo, W, L = C_2H_4; M = W, L = C_3H_6), as well as others and have interpreted the results in terms of a MO model which takes the level scheme for $(\eta\text{-}Cp)_2M$ (D_{5h} symmetry) and determines level changes as the angle between the (η-Cp) rings is increased from zero degrees (molecular symmetry is lowered to C_{2v}).[397] Hillier et al. have carried out all-electron SCF molecular orbital calculations for $(\eta\text{-}C_6H_6)_2Cr$ and $(\eta\text{-}C_6H_6)Cr(CO)_3$, and the He(I) and He(II) PES were given, and compared to the theoretical results. The latter indicate that the η-arene rings bear negative charges, and that there is a transfer of electron density via π-orbitals to CO in comparing $Cr(CO)_6$ to $(\eta\text{-}C_6H_6)Cr(CO)_3$.[398] Galyer, Wilkinson and Lloyd have reported He(I) and He(II) PES for Me_6W. The results are consistent with octahedral symmetry in this molecule. Evidence indicates that W-C bonding is mainly d and s in character, and that there is steric interaction between Me groups in this molecule. The PES also indicate that the previously-reported PES spectrum for this molecule (AS 1972/311) was in fact the PES of a molecule other than Me_6W.[399]

Charge-transfer complexes formed between (η-arene)$M(CO)_3$ complexes (arene = C_6H_5Me, o, m, p-$C_6H_4Me_2$ and 1,3,5-$C_6H_3Me_3$) and 1,3,5-trinitrobenzene (TNB) and tetracyanoethylene (TCNE) have been studied. Complex formation between TNB and the metal complex is observed for Cr, but not for Mo or W, while it is observed for all three metals for TCNE. The charge transfer interaction with TMB is held to involve a face-to-face stack of arene rings, while for TCNE, it is an inner-sphere interaction between the acceptor and metal. The PES spectra for (η-arene)$Cr(CO)_3$ complexes (arene = toluene, mesitylene, dimethylaniline) are also given.[400]

Induced circular dichroism absorption of $W(CO)_6$ in cholesteric solvents has been measured and discussed,[401] and magnetic circular dichroism in $Cr(CN)_5(NO)^{3-}$ has been studied.[402]

Infrared and Raman spectra. The availability of more sophisticated instrumentation is facilitating studies of increasing detail. A method of determining the extent to which the Cotton-Kraihanzel (C-K) "neglect of anharmonicity corrections" approximation for $M(CO)_xL_{6-x}$ molecules is valid has been studied. In this method each set of non-equivalent M-C-O groups is treated as a separate diatomic molecule, and the anharmonicity corrections are determined through application of simple diatomic potential functions. It has been found that anharmonicity corrections are about constant over a narrow range of force constants, and vary systematically over a more extended range. Thus neglect of anharmonicity corrections is a valid approximation for C-K systems, in which these conditions apply.[403]

Several studies of the hexacarbonyls have been reported. Kovalenko and coworkers have calculated force constants for $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ by a method which does not involve reducing the energy matrices with respect to symmetry. The results were in good agreement with those obtained through application of conventional techniques.[404] The influence of coriolis coupling of triply-degenerate vibrations of spherical top molecules on autocorrelation functions has been studied theoretically, and the results have been applied to $M(CO)_6$ (M = Cr, Mo) in gaseous N_2 and in liquid CCl_4[405]. The Raman spectra for polycrystalline $M(CO)_6$ (M = Cr, Mo, W) have been investigated in the 4000 cm^{-1} region. It was concluded that factor group splitting is not important in this ν(CO) overtone region, and that the harmonic pattern of bands in this region for a crystalline material cannot, in general, be predicted by summing the frequencies of the corresponding fundamental modes when the latter show factor group splitting.[406]

Low frequency spectra for $Cr(CO)_6$ and $Mo(CO)_6$ in argon, nitrogen and oxygen matrices at 15° K have been obtained by Tevault and Nakamoto.[407] For bands at 670 and 600 cm^{-1} respectively which had been assigned as predominantly M-C-O bending modes (*AS* 1969/255) metal isotopic structure for the bands was observed in the N_2 matrix. Thus there is coupling of δ(MCO) and ν(MC) in these vibrations. The observed structure has been simulated by computer, and the results have allowed a more complete force-field calculation for the T_{1u} symmetry species to be carried out.[407]

Band assignments have been determined and a normal coordinate analysis which employed a general quadratic valence potential field has allowed a description of the normal modes and calculation of force constants for $(PH_3)M(CO)_5$ (M = Cr, Mo,-W) on the basis of infrared and Raman data.[408] The results indicate that phosphine exercises an almost identical influence on the M-C-O groups *cis* and *trans* to it. Infrared and Raman spectra for the solid state and for solid solution (85° K, ethanol/ether/isopentane), which included assignment of isotopic satellites, have permitted the identification of intramolecular force constants (for contiguous molecules) for *trans* - $Mo(CO)_4(PEt_3)_2$.[409] Solid state and solution IR and laser Raman data in the CO and NO stretching regions, and below 750 cm^{-1}, which also included assignment of ^{13}C satellite peaks, support a *trans* structure for $W(CO)_4(NO)(Br)$. The assignment has been confirmed through energy factored force field calculations.[410]

Infrared stretching frequencies have been obtained for the linear trimetallic $[M''\text{-}Au\text{-}M'']^-$ groups for M'' = $(\eta\text{-}Cp)Mo(CO)_3$ and other metalloorganic substituents. The data are correlated for a variety of M''-M'-M'' groups on the basis of the oxidation states and coordination geometry of M' (*cf.* refs. 185,187).[186]

Ellermann and coworkers have obtained infrared and Raman spectra for the ligands (L = $C(CH_2EPh_2)_4$; E = P, As)) and for their $LM(CO)_3$ complexes in the region 2000-150 cm^{-1}. All L vibrations, and $\nu(CO)$, $\delta(MCO)$, $\nu(MC)$ and $\nu(ME)$ in the complexes have been assigned.[411]

Infrared and Raman spectra (to 33 cm^{-1}) have been reported for $(OC)_5ReM'(CO)_5^-$ (M' = Cr, Mo, W) and have allowed force constant determinations for these molecules.[412] The k(ReM') were found to vary W>Mo>Cr. Comparisons of the stretching force constants for the Mn analogues, and for $M_2(CO)_{10}$ species (M = Mn, Re) were made; the neutral species have the higher metal-metal stretching force constants. Assignments for the MeC_5H_4 vibrational modes in $[(\eta\text{-}MeC_5H_4)Mo(CO)_3]_2$ have been made on the basis of solid state (Raman and infrared) and solution (infrared) spectra. The MeC_5H_4 group exhibits C_s symmetry in this complex.[413]

Several studies of (η-arene)-containing complexes also have been reported. Rudnevskii and associates have studied the infrared spectra of $[(\eta\text{-}\underline{p}\text{-}RC_6H_4)Cr(CO)_3]_2Hg$ (R = H, F, Me, MeO, Me_2N, CO_2Et) and have correlated the results with Hammett substituent constants,[414] and the same group has also studied the infrared spectra for $(\eta\text{-}XC_6H_5)Cr(CO)_3$ complexes (X = NMe_2, Me, OMe, H, F, Cl, I, COOEt).[415] The ν(Cr-C) are less affected by the donor-acceptor properties of X than are $\nu(CO)$, while $\delta(CrCO)$ are not influenced by X. Other such comparisons for this series of complexes are also discussed.[415]

Approximate vibrational analyses for $(\eta\text{-}C_6H_6)Cr(CO)_3$ and its deuterated analogue have been given by Adams, Christopher and Stevens. In contrast to the earlier proposal of Cyvin *et al.* (*AS* 1972/270,271) it is concluded that kinematic coupling effects do not account well for shifts in ring frequencies upon complexation. Descriptions of the normal modes were given.[416]

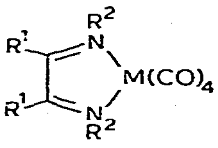
Carbonyl stretching force constants and interaction constants for solid $(\eta\text{-}C_6H_6)Cr(CO)_3$ have been determined by three methods, based upon fundamental band frequencies, infrared band intensities, and molecular force constants derived from the positions of satellite ^{13}C isotopic vibrations, employing both infrared and Raman data in several media at 85^o K, by Bigorgne *et al.*.[417] The last two methods were judged to be the most useful.

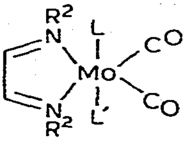
Infrared spectra (solution and solid state) have been determined for $(\eta\text{-}C_6H_6)M(CO)_3$ and $(\eta\text{-}1,3,5\text{-}Me_3C_6H_3)M(CO)_3$ (M = Cr, Mo, W) over the range 4000 - 250 cm^{-1}, and the bands have been assigned. It is concluded that substituent electronic effects are inductive in nature. Metal-ring force constants were found to vary Mo<Cr<W, while metal-CO force constants increased in the order Cr<Mo<W. The Mo and W, but not the Cr complexes can be protonated reversibly at the metal atom in CF_3COOH solution; protonation is more facile for the mesitylene complexes.[418]

A single crystal Raman study of the isomorphous $(\eta\text{-}Me_6C_6)\text{-}Cr(CO)_3$ and $(\eta\text{-}Me_5C_6H)Cr(CO)_3$ complexes indicated that the vibrational factor group approach offered the simplest explanation for the main features in the 2000 cm^{-1} spectral region. Explanations for some observations, however, lie outside a simple harmonic oscillator-factor group approach.[419] The vapor phase molecular structure of $(\eta\text{-}C_6H_6)Cr(CO)_3$ has been determined by electron diffraction,[31] and these results, together with vibrational calculations, indicate the molecule to be nearly an unhindered internal rotor. Its vapors consist of a mixture of several conformers which differ by rotational arrangement with respect to the $\text{-}Cr(CO)_3$ moiety. States other than the eclipsed or staggered may be significantly populated, but the energy barriers to rotation could not be determined since the ratios were uncertain. The gas phase results may be contrasted to the solid-state configuration, in which the carbonyls are staggered relative to the ring-carbons.[31]

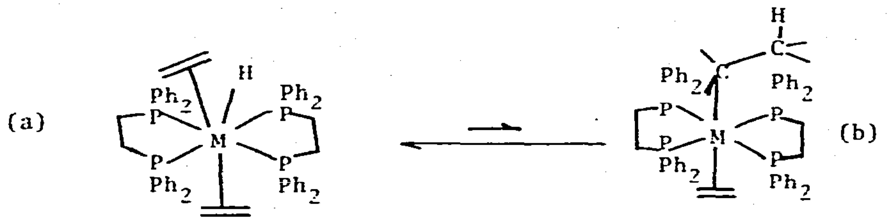
Several reports have taken advantage of spectral relationships among similar molecules. Thus Lokshin _et al_. have compared the infrared and Raman spectra (solid state and solution, 4000-250 cm^{-1}) of $(\eta\text{-thiophene})Cr(CO)_3$ to that of $(\eta\text{-}C_6H_6)Cr(CO)_3$, and have concluded that benzene and thiophene are similar as π-bonding ligands.[420] Caillet has reported a complete vibrational analysis for $(\eta\text{-methylbenzoate})Cr(CO)_3$, and has determined a valence force field for the molecule, employing the force fields of methyl benzoate and $Cr(CO)_6$. Thus the perturbations which accompany complexation were made evident. The results demonstrate that vibrations at lower frequencies are strongly coupled, with the exception of $\delta(CrCO)$, but that $\nu(CO)$ are relatively pure.[421] In two reports, Caillet has also calculated force constants for $(\eta\text{-}C_6H_5COOMe)Cr(CO)_2(CS)$ with the assistance of data for the analogous $(\eta\text{-}C_6H_5COOMe)Cr(CO)_3$ complex. The infrared and Raman data for Nujol were taken over the range 4000-2000 cm^{-1} (IR) and 3500-20 cm^{-1} (Raman).[422,423]

Nuclear magnetic resonance and Mössbauer spectra. Proton NMR and long-range coupling constants have been determined for a variety of glyoxaldiimine complexes (CXXII) (M = Mo, W; R^1 = H; R^2 = Me, *cyclo*-C_3H_5, Pr^i, Bu^t, *cyclo*-C_6H_{11}, CH_2Ph, Ph, *o*-C_6H_4Me, *p*-C_6H_4Me, *p*-C_6H_4OH, *o*,*o*'-$C_6H_3Me_2$, *o*, *m*-$C_6H_3Me_2$, NH_2; R^1 = H, Me, R^2 = *cyclo*-C_6H_{11}), together with more highly-substituted complexes (CXXIII; L = CO, L' = PPh_3, CH_3CN; L = L' = PPh_3, $PBu^n{}_3$). Additionally the ESR spectra for some corresponding anion radicals have been obtained and discussed.[424]


(CXXII)

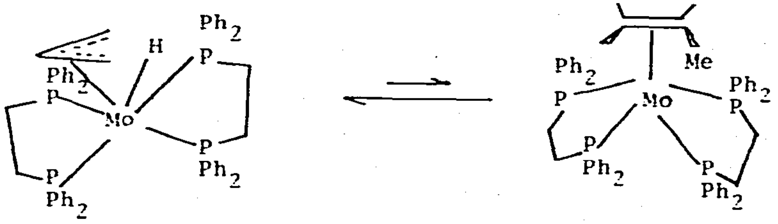

(CXXIII)

Kreiter and Strack have prepared *cis*-$W(CO)_4(PPh_3)(L)$ complexes (L = *cis*- and *trans*- $MeOOCCH{=}CHCOOMe$, $CH_2{=}CH_2$) *via* uv-irradiation of $W(CO)_5(PPh_3)$ in THF and addition of L, and studied hindered rotation of L *via* variable-temperature proton NMR spectroscopy. Favorable orientations of L relative to the coordination octahedra were determined, and ΔG^* values for the process reported.[425] Similar studies for (η-Cp)Cr(CO)(NO)(L) (for L other than $CH_2{=}CH_2$) by Kreiter and coworkers indicated that restricted rotation about the Cr-olefin bond was the only molecular reorientation to 120°C. The data also indicate L to be preferentially oriented so that the double bond is parallel to the plane of the Cp ring. Possible stereoisomers were discussed, and values of ΔG^* were presented.[426] The proton NMR spectra of (η-*p*-$MeC_6H_4\overset{+}{C}HMe)Cr(CO)_3$ and (η-*p*-$(MeC_6H_4)_2\overset{+}{C}H)Cr(CO)_3$ and the corresponding arenes together with those of the corresponding alcohols have been recorded in HSO_3F at -50°. Comparison of the spectra support a charge migration toward the metal in the (η-arene) cations, which stabilizes the carbonium ions.[427] Broad-line NMR spectra for crystalline (η-$C_6H_6)Cr(CO)_3$ have been recorded as a function of temperature, and T_1 and line-width measurements were made to study possible hindered rotation of the ring. The data indicated that most of the hindrance resulted from the crystal environment, rather than from intramolecular forces.[428] Osborn and coworkers have reported direct observation of reversible hydrogen-exchange processes of importance to the mechanism of catalytic processes, employing variable-temperature ^1H NMR spectroscopy. The complexes (29-a), prepared through treatment of *trans*-$(diphos)_2M(N_2)_2$ (M = Mo, W) with ethylene and CF_3COOH or by other means undergo the exchange process (29), and thus provide direct evidence of insertion-deinsertion of hydrogen.



(29)

With propylene instead of ethylene, (HMo(η-C_3H_5)(diphos)$_2$, obtained *via* treatment of $MoCl_3 \cdot (THF)_3$ with Na/Hg in THF under propylene), the exchange process (30) was



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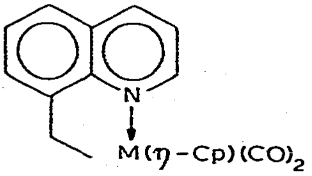
observed, an example of the mechanism proposed to occur for 1,3-hydride shifts found in many metal-catalyzed olefin reactions.[429]

Carbon-13 NMR spectra for an extensive series of $L_nM(CO)_{6-n}$ complexes (n = 0, 1, 2; M = Cr, Mo, W; L = PPh_3, PCl_3, $P(OPh_3)$, $P(OMe)_3$, PH_3, PPh_3, $AsPh_3$, $SbPh_3$, PEt_3, PBu_3, NH_2(*cyclo*-C_6H_{11}), NHC_5H_{10}, Cl^-) have been reported by Bodner and Gaul.[430,431] It was observed that CO's *trans* to L were deshielded relative to *cis* CO's, and that Mo and W shield carbonyls relative to Cr. The latter observation was attributed to contributions to the chemical shift by neighboring diamagnetic screening. A linear relationship was observed between the *cis* carbonyl stretching force constant k_2 and *cis* CO chemical shifts; while *trans*-$^2J^{13}C^{31}P$>*cis*-$^2J^{13}C^{31}P$ for Mo and W, the reverse is true for Cr. The data indicate that carbonyl chemical shifts and $^2J^{13}C^{31}P$ for $L_2M(CO)_4$ and $L_3M(CO)_3$ can be predicted on the basis of data for $LM(CO)_5$.[430] The signs of the one, two and three-bonded ^{13}C-^{31}P coupling constants for $Ph_3PMo(CO)_5$ have been determined to be positive.[431] Senoff and Ward have studied the ^{13}C NMR spectra of a series of phenylthiocarbenepentacarbonyltungsten(O) complexes, ($\underline{p}$-XC_6H_4S)(Me)CW$(CO)_5$ (X = OH, OMe, Me, F, H, Br), as well as those of the parent thiols. The data support both σ- and π-interactions between the ring and carbene carbon.[432] ^{13}C-^{183}W coupling constants, which are sensitive to hybridization at carbon, have been employed as a diagnostic probe of metal-carbyne, metal-carbene and metal-alkyl bonding in carbonyl complexes,[433] and the existence of a metal-carbon σ-bond in (CXIV), and in other, related complexes has been demonstrated by ^{13}C NMR spectroscopy.[434]

Howell and Trahanovsky have studied the ^{13}C FT NMR spectra for benzonorbornadiene (LXXXVIII, a), (η^6-benzonorbornadiene)-$Cr(CO)_3$ (b) and (η^8-benzonorbornadiene)$Cr(CO)_2$ (c) ($\underline{cf}$. refs. 234, 235), to ascertain changes in the steric and electronic properties accompanying the successive conversion of (a) to (b) to (c). The data support little distortion of (a) upon complexation, but significant distortion upon ring-closure in (b) to afford (c). Data indicate the olefinic group in (c) to be strongly π-accepting, and strongly bound to Cr.[435]

The variable-temperature ^{13}C NMR spectra of (η-guaiazulene)-$Mo_2(CO)_6$ (CXXV) have revealed that local scrambling of carbonyls bonded to each metal atom proceeds at different rates, with a difference in activation energy of $\underline{ca}$. of 4-5 kcal/mole. No intermetallic scrambling of the carbonyls is observed.[436] The carbon-13 NMR spectra for a series of (η-arene)$Cr(CO)_3$ complexes, together with those of the free ligands (arene = C_6H_5X, X = H, Me, Pr^i, Bu^t; $\underline{m}$-$C_6H_4X_2$, X = Me, Bu^t; and 1,3,5-$C_6H_3X_3$, X = Me, Bu^t) have revealed that conformers in which the ring-substituents are staggered relative to the carbonyls are favored as the size of X increases, but that there is observed no restriction of rotation of the arene group to -60°.[437] Electronic effects are



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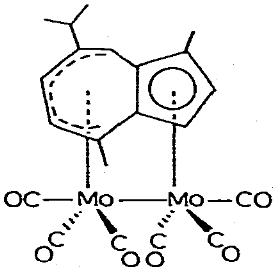
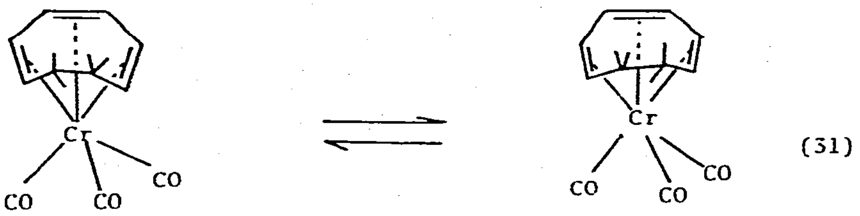


(CXXV)

consistent with those reported by Todd and Bodner (AS 1974/313).

Free energies of activation for hindered rotation about the three fold axis of the -M(CO)$_3$ group in a series of (η-polyene)M(CO)$_3$ complexes (polyene = 1,3,5-cycloheptatriene, 1,3,5-cyclooctatriene and 1,3,5,7-cyclooctatetraene; M = Cr, Mo) have been determined through use of ^{13}C NMR spectroscopy. For (η-1,3,5-cyclooctatriene)Cr(CO)$_3$ at -120°, the complex was found to be frozen in a chiral position. The free energy of activation for the interconversion of the enantiomers (31) was also determined.[438] Köhler has reported assignments for the FT ^{13}C NMR spectra for a series of metallocenes substituted by phenyl and ethyl groups, including (η-EtC$_5$H$_4$)$_2$Cr.[439]


(31)

Garrou has presented ^{31}P NMR data for cis-(P$_2$)M(CO)$_4$ complexes (P$_2$ = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1-3), PPh$_2$Bu^n, M = Cr, Mo, W; P$_2$ = PPhBu^n$_2$, PPh(CH$_2$CH$_2$CH=CH$_2$)$_2$, M = Mo) and related complexes of other metals, and has concluded that a ring contribution to the coordination chemical shift exists in these and other phosphorus chelate complexes.[440] The systematics of ^{31}P NMR spectra for a variety of metal complexes, including those of Cr, Mo and W carbonyls, of several polytertiary phosphines (Me$_2$PCH$_2$CH$_2$PPh$_2$ (= P$_m$P$_f$), P$_m$P$_m$P$_m$, P$_m$P$_m$P$_f$ and P$_f$P$_f$P$_f$), have been reported by King and Cloyd. Complexed vs. uncomplexed P are readily differentiated.[441] Isaacs and Graham have unequivocally distinguished between fac- and mer-(Ph$_2$PCH$_2$PPh$_2$)$_2$Mo(CO)$_3$ on the basis of their ^{31}P NMR spectra.[442] The ^{31}P spectra of (η-arene)-Cr(CO)$_2$PPh$_3$ complexes in neutral and acidic (CF$_3$COOH) media (arene = C$_6$H$_5$X (X = H, Me, OMe, NMe$_2$, COOMe), p-C$_6$H$_4$(COOMe)$_2$, 1,3,5-$C_6H_3Me_3$) have been employed to determine the degree of protonation, which was found to increase with decreasing temperature.[443]

Studies of ^{19}F chemical shifts of fluoroarenes, both free, and complexed to -$Cr(CO)_3$ (arene = m, p-FC_6H_4X; X = H, F, Cl, Me, OMe, NH_2, CF_3), have revealed that transmission of resonance effects within the ring systems differ little in the free and complexed arenes, but that inductive effects are greatly diminished.[444]

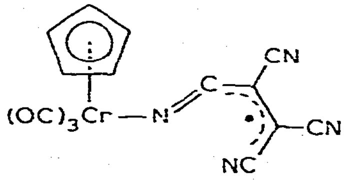
Magnetic shieldings for ^{119}Sn have been determined through heteronuclear double resonance experiments for thirty-five organotin complexes containing transition metals (including thirteen containing Cr, Mo, or W).[445]

Three investigations of ^{119}Sn Mössbauer spectroscopy on complexes containing Sn bonded to Cr, Mo or W have been reported. Kruck and coworkers have described Mössbauer results for $M(CO)_{6-x}L_x^{-x}$, $x = 1,2,3,6$; L = SnX_3^-) complexes ($M(CO)_5(L^-)$ (L^- = $SnCl_3^-$, SnF_2Cl^-, M = Cr, Mo, W; $M(CO)_5(SnBr_3^-)$, M = Mo, W; $Mo(CO)_5(SnCl_2Br^-)$, $Cr(CO)_4(SnCl_3^-)_2$, $M(CO)_3(SnCl_3^-)_3$ (M = Mo, W); $Cr(SnCl_3^-)_6$). Increasing substitution of CO by SnX_3^- affords greater π-bonding of the metal to Sn; the π-accepting ability of $SnCl_3^-$ is approximately the same as that of PCl_3. A direct relationship was observed between the isomer shift (δ) and the electronegativity of X, while an inverse relationship between δ and the quadrupole splitting (Δ) was also noted.[446] A ^{119}Sn Mössbauer study of $L_2M(CO)_3(SnR_{3-n}Cl_n)(Cl)$ has been reported by Cullen and coworkers (R = Me, Ph, L_2 = dipy, phen, DTH; M = Mo, W, n = 1-3). The results indicate W to be a better σ-donor than Mo. In (dipy)$Mo(CO)_3(SnR_2Cl)(Cl)$ it is inferred that Mo and two C (in R) atoms occupy approximately equatorial positions in the distorted trigonal bipyramidal environment about tin. Partial dissociation of (dipy)$Mo(CO)_3(SnI_3)(I)$ to (dipy)$Mo(CO)_3$-(I)(I) and SnI_2 is also noted, on the basis of the data.[447]

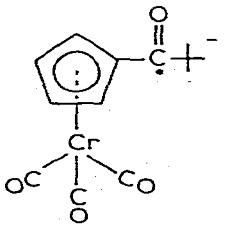
A point charge method has been employed to analyze quadrupole splitting data from the Mössbauer spectra (^{119}Sn and ^{57}Fe) for $(X_3Sn)M(CO)_3(\eta\text{-}Cp)$, $(X_2Sn)[M(CO)_3(\eta\text{-}Cp)]_2$ and (X_2Sn)-$[M(CO)_3(\eta\text{-}Cp)][Fe(CO)_2(\eta\text{-}Cp)]$; discrepencies between the model and the experimental results are discussed, and a correlation between the electric field gradient at the Sn nucleus and $\nu(CO)$ is noted.[448]

<u>Electron spin resonance spectra</u>. Glyoxaldiimines and their tetracarbonyl molybdenum(0) complexes (CXXII; R^1 = H, R^2 = Bu^t,

Pr^i, Bu^i; R^1 = H, Me, R^2 = Me, CH_2Ph, Pr^i, $C_6H_{11}{}^c$, $C_3H_5{}^c$) and their tetracarbonylmolybdenum(0) complexes react with K to give stable, paramagnetic anions, for which high resolution ESR spectra are given. The conformations of R^2 in the free and complexed ligands are compared and discussed (cf. refs. 146,424).[449] The oxidative cleavage of $[(\eta\text{-}Cp)Cr(CO)_3]_2$ and $[(\eta\text{-}Cp)Cr(CO)_3]_2Hg$ by TCNE to afford (CXXVI), stable only below -25° has been studied employing ESR spectroscopy.[450] Complexes of the type $[(\eta\text{-}Cp)_2M(X)(Y)^+]\ PF_6{}^-$, formed through chemical or electrochemical oxidation of $(\eta\text{-}Cp)_2M(X)(Y)$ or exchange reactions in which X and Y are formal one-electron donors such as (Br)(Cl), $(Br)_2$, (NHC_6H_4S), $(NCS)_2$, $(N_3)_2$, (O_2CCF_3), (NHC_6H_4O), O_2CPh and M = Mo, W, have been studied by ESR spectroscopy. The <g> values and solution hyperfine coupling constants are given and discussed.[451] Vansant has prepared $(\eta\text{-}Cp)_2Cr^+$ in aqueous solution and exchanged it into zeolite, and obtained its ESR spectra. Spin concentrations and <g> values for this and related complexes containing other metals are given.[452] The ESR spectrum of (CXXVII) has also been given and discussed by Ceccon and associates.[453]



(CXXVI)



(CXXVII)

Mass spectra. It had been noted that heats of formation of metal ions determined mass spectrometrically exceed those determined by spectroscopic methods, and, for $M(CO)_6$ (M = Cr, Mo, W) it had been suggested that the difference ("excess energy") resulted from the formation of metal ions in excited states. It is pointed out by Davis, however, that that explanation appears to violate quasi-equilibrium theory, which assumes that initial excitation energy randomizes throughout the molecule at a rate rapid relative to bond dissociation. Data for the $M(CO)_6$ systems are consistent with an alternative explanation, that the "excess energies" represent kinetic shifts, i. e., are the energy excesses required to allow the mass spectrometric reactions to proceed at rates appropriate to the mass spectrometric time scale.[454]

Differential thermal analysis, thermogravimetric analysis, and mass spectral data for (benzilbis(phenylimine))Mo$(CO)_4$ have been interpreted in terms of a strong π-acidity of the ligand.[455] The ionization and thermal decomposition of $[(\eta\text{-Cp})W(CO)_3]_2$ have been measured by mass spectrometry.[456] Appearance potentials for the principal ions, and the change in enthalpy for the equilibrium between the dimer and the two identical monomeric fragments have been determined.[456] The field desorption mass spectra, which can be obtained for relatively involatile materials, have been recorded for $(\eta\text{-}C_6H_6)Cr(CO)_3$ and $[(\eta\text{-}C_7H_7)W(CO)_3^+]BF_4^-$. In each case the molecular or quasi-molecular ion was observed, and fragmentation patterns determined.[457]

Davis has noted that the fragmentation of $(\eta\text{-}C_6H_5COOR)Cr(CO)_3$ by loss of ·OR is an exception to an otherwise good generalization by McLafferty that odd-electron fragments are generally less stable, and thus less observed, than even-electron fragments in mass spectra.[458] Blake et al. have observed secondary electron-capture in the negative ion mass spectra of both $(\eta\text{-}C_6H_5COOH)Cr(CO)_3$ and $(\eta\text{-}C_6H_5COOMe)Cr(CO)_3$ which results in decarbonylation of the -COOR function. Cr^- ions were also observed.[459] Müller, Holzinger and Kalbfus have reported evidence for binuclear secondary ions formed during the fragmentation of $(\eta\text{-Cp})(\eta\text{-}C_6H_6)Cr$ and $(\eta\text{-Cp})(\eta\text{-}C_7H_7)Cr$. Their formation, and fragmentation patterns are discussed.[460] Two means of fragment stabilization, (a) via redistribution of excess energy among the covalent bonds, and, (b) by structural distortion, were deduced from a comparison of quantum-mechanical calculations and experimental data for $(\eta\text{-}C_6H_6)_2Cr$ and $(\eta\text{-}C_6H_6)Cr(CO)_3$.[461] Finally, the field ionization mass spectra for $(\eta\text{-arene})_2CrI$ species (arene = C_6H_6, EtC_6H_5 and $Et_2C_6H_4$) have been employed in the analysis of trace amounts of these complexes.[462]

Electrochemistry

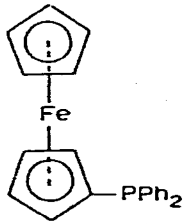
Reduction of $M(CO)_6$ at a Pt electrode in aprotic solvents to afford $M_2(CO)_{10}^{-2}$ (M = Cr, Mo, W) has been studied, and the systematics of the potential discussed (cf.refs. 284, 285). Oxidation of $Cr(CO)_6$ in acetonitrile affords $Cr(CO)_6^+$, stable on the seconds time scale.[463] Electrochemical measurements on octahedral metal carbonyls, including $Cr(CO)_4(NCCH_3)_2$,

$Cr(CO)_5Br^-$, $Cr(CO)_5(NCCH_3)$, $Cr(CO)_6$ and others containing V or Mn have been reported.[464] E^o values from cyclic voltammetry in $CH_3CN/0.2$ M Bu_4NBF_4 (vs. $(\eta\text{-}Cp)_2Fe/(\eta\text{-}Cp)_2Fe^+$ couple) obey the relationship,

$$E^o = A + x\,\frac{dE^o}{dx} + 1.48^o y, \qquad (32)$$

where A is a constant depending on the solvent and reference potential, x and y are given in $[M(CO)_{6-x}L_x]^{Y+}$, and $(dE^o/dx)_L$ is a parameter characteristic of L which defines the shift in E^o caused by replacement of one CO by one L. Eq. (32) allows estimation of E^o for hexacoordinate metal carbonyls, or can assist in structure determination.[464]

Kotz and coworkers have prepared the new $L_2M(CO)_4$ complexes (L = $FcPh_2P$ (CXXVIII), Fc_2PhP, Fc_3P; M = Mo, W) directly, and have studied the electrochemical reduction of these and of $LM(CO)_5$, as well as of other L-containing complexes. The reductions were reversible, one electron processes; the systematics of the results were discussed.[465] Electrochemical reduction of ten $(\eta\text{-arene})Cr(CO)_3$ complexes at a dropping Hg electode in DMF has revealed that electron donating substituents on the arene ring shift the reduction potentials to more positive values. The two-electron reduction of $(\eta\text{-}C_6H_6)Cr(CO)_3$ is reversible and proceeds through formation of an intermediate anion radical.[466] Pulse polarographic data for variety of tricarbonylchromium π-complexes of arenes and condensed aromatics (naphthalene derivatives) also has revealed that reduction is a two-electron process; reduction of $(\eta\text{-}CH_3COC_6H_5)Cr(CO)_3$ in contrast, is a one-electron process.[467]



(CXXVII)

Thermochemistry

There is developing an increasing interest in the determination of the thermodynamic properties of organometallic complexes, and this interest is reflected in appreciable work in this area reported during 1975. Several groups have reported the thermodynamic properties for the hexacarbonyls; standard enthalpies of formation for $Cr(CO)_6$,[468,469,470] $Mo(CO)_6$,[470] and $W(CO)_6$.[470] Other thermodynamic properties for the hexacarbonyls, e. g., heats of combustion,[468,469,471] heat capacities,[470] entropies,[470] and free energies of formation[470] have also been reported. The heat of combustion, together with the heat of thermal decomposition for $Mo(CO)_6$, the heat of reaction of $Mo(CO)_6$ with I_2 and other data were employed in the determination of the standard heats of formation of MoI_2 and MoI_3.[471] Standard heats of formation have also been determined for $(CH_3CN)W(CO)_5$, cis-$(CH_3CN)_2$-$W(CO)_4$ and fac-$(CH_3CN)_3W(CO)_3$ employing differential scanning calorimetry and an automated vapor pressure measurement apparatus. Thermal stabilities have been found to decrease in the order $W(CO)_6 > (CH_3CN)_3W(CO)_3 > (CH_3CN)_2W(CO)_4 > (CH_3CN)W(CO)_5$.[472] Another calorimetric study has determined the standard heat of combustion, the standard heat of formation, and the mean Cp-Cr bond dissociation energy for a variety of bis(η-Cp)metal complexes, including $(\eta\text{-Cp})_2Cr$.[473] Yet another investigation has reported C_p, S, the enthalpy function and the free energy function for this complex from 5 to 298.15° K.[474] Standard heats of formation also have been determined for (η-toluene)$Cr(CO)_3$, (η-mesitylene)-$Cr(CO)_3$ and (η-chlorobenzene)$Cr(CO)_3$; the (η-arene)-Cr bond contributions in the gas phase, based on these and other data, vary $C_6Me_6\text{-}Cr \gg 1,3,5\text{-}C_6H_3Me_3\text{-}Cr > C_6H_5Me\text{-}Cr > C_6H_6\text{-}Cr > C_6H_5Cl\text{-}Cr >$ cyclo-C_7H_8-Cr.[475] A new, simple microcalorimetric vacuum-sublimation technique, accurate to ±5% was employed in the determination of heats of sublimation at 298° K for a variety of (η-arene)$Cr(CO)_3$ complexes (containing the arene ligands listed in the previous sentence), and for $Cr(CO)_6$ and $W(CO)_6$.[475]

The stabilities and bond strengths for a variety of Hg(II) halide adducts of Group VI-B metal carbonyl derivatives have been studied by microcalorimetry in 1,2-dichloroethane.[476] The following reactions were studied: (η-mesitylene)$M(CO)_3$ with HgX_2 (M = W, X = Cl, Br; M = Cr, Mo, X = Cl), (η-methyl benzoate)-$Cr(CO)_3$, (η-methyl-p-aminobenzoate)$Cr(CO)_3$, (2,2'-dipyridyl)Mo-$(CO)_4$, (diphos)$M(CO)_4$ (M = Cr, Mo, W), and $(diphos)_2Mo(CO)_2$ with $HgCl_2$. Enthalpies and entropies of adduct formation were determined, and higher enthalpies of adduct formation were observed for Mo and W complexes than for Cr complexes, an observation attributed to the greater availability of non-bonding electrons for the larger metal atoms. A large, favorable entropy effect for Cr complexes relative to those of Mo and W was held as possibly arising from displacement of solvent molecules due to more compact adduct structure for the Cr systems. For (diphos)$M(CO)_4$ (M = Cr, Mo) the results suggested loss of CO prior to adduct formation, perhaps catalyzed by $HgCl_2$. The observed entropies of adduct formation were slightly greater than for Hg(II) adducts of "conventional" Lewis bases, indicative of relatively strong Hg-transition metal bonds.[476]

A number of groups have studied the thermal decomposition of organometallics. Syrkin and coworkers have prepared Cr coatings of various qualities through thermal decomposition of $Cr(CO)_6$.[477] Krichevskaya and associates have studied the removal of C and O impurities from $W(CO)_6$ employing several methods,[478] while Komorova and Jaluvka performed thermodynamic calculations for the ternary system W, C, O at 600-1000° K to determine the conditions under which tungsten carbide could be prepared through the decomposition of tungsten hexacarbonyl.[479]

Mohai and Bencze have studied the thermal decomposition of $M(CO)_nL_2Cl_2$ (M = Mo, W; L = PPh_3, $AsPh_3$, $OPPh_3$; n = 2,3), and have found that the tricarbonyl complexes lose two, then one mole of CO, and then lose L in a multistep process. With the dicarbonyls, either one- or two-step loss of CO is observed, depending upon the identity of L. The thermal stabilities of the complexes vary W>Mo; $PPh_3>AsPh_3>OPPh_3$; dicarbonyl>tricarbonyl.[480,481] These workers have also prepared $M(CO)_2Cl_2(OPPh)_2$ (M = Mo, W), and have compared their thermal decomposition to that observed for $M(NO)_2Cl_2L_2$ (L = PPh_3, $OPPh_3$, $AsPh_3$), which undergo intramolecular redox reactions with evolution of N_2 or N_2O and oxidation of M or L. For the carbonyl complexes, in contrast, loss of two carbonyls at ca. 160° was noted, but above that temperature, no horizontal weight levels were observed in the TG's.[482]

The activation energies for the thermal decomposition of (η-arene)$_2$Cr (arene = benzene, ethylbenzene) have been determined to be ca. 22.5 kcal/mole.[483] Another study has fixed attention upon the nature of coatings precipitated from the vapor phase during thermal decomposition of (η-arene)$_2$Cr complexes,[484] while another investigation has developed an equation which can be used to determine the decomposition rate of (η-arene)$_2$Cr on a substrate oriented perpendicularly to the carrier gas flow, as a function of carrier gas flow, the concentration of the organometallic in the carrier gas, and temperature. Good results were obtained employing (η-ethylbenzene)$_2$Cr and (η-ethylbenzene)-(η-diethylbenzene)Cr as substrates.[485]

The decomposition of $Me_3SiCH_2WCl_5$ at 20° has been found to afford Me_3SiCl, Me_3SiCH_2Cl, $Me_3SiCH_2CH_2SiMe_3$ and Me_4Si. The first-named product evidently is formed via elimination of $CH_2{=}WCl_4$ from the substrate.[486]

The cosolubilities of (η-C_6H_6)$_2$CrI, (η-$Me_2C_6H_4$)$_2$CrI, (η-mesitylene)$_2$CrI and (η-MeC_6H_5)$_2$CrI have been found to remain virtually constant in water over 10-40°C.[487]

Miscellaneous

Ion-cyclotron resonance line-broadening has been employed to determine experimentally the momentum transfer rate for collisions of $Cr(CO)_5^-$ ions with isotropic and anisotropic polar and non-polar gases. The Langevin theory (which describes gas-phase ion-molecule collisions on the basis of potential energy functions for ion-molecule attractive and repulsive forces) is found to be well-obeyed.[488]

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