CHROMIUM, MOLYBDENUM, AND TUNGSTEN

ANNUAL SURVEY COVERING THE YEAR 1976 *

JIM D. ATWOOD AND MARY L. ATWOOD

DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK AT BUFFALO,
BUFFALO, NEW YORK 14214 (U.S.A.)

MARCETTA Y. DARENSBOURG AND DONALD J. DARENSBOURG

DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY,
NEW ORLEANS, LOUISIANA 70118 (U.S.A.)

CONTENTS

---

*Previous review see J. Organometal. Chem., 143 (1977) 385 - 487.

ABBREVIATIONS

acac - acetylacetonate
bipy - bipyridine
Bu - n-butyl
t-Bu - t-butyl
COT - cyclooctatriene
Cp - cyclopentadienyl
dam - bis(diphenylarsino)methane
das - o-phenylenebis(dimethylarsine)
dppe - 1,2-bis(diphenylphosphino)ethane
dmpe - 1,2-bis(dimethylphosphino)ethane
dpm - bis(diphenylphosphino)methane
Et - ethyl
Me - methyl
o-phen - o-phenanthroline
piper - piperidine
Pr - propyl
i-Pr - isopropyl
Pz - pyrazine
TMEDA (tmen) - tetramethylethylenediamine

REVIEWS

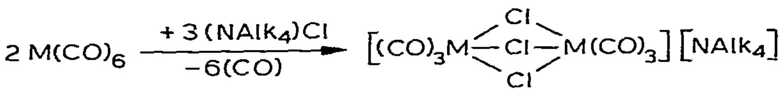
Reviews covering the following areas of chemistry appeared in 1976: The thermodynamic properties, chemical equilibria and standard potentials of chromium, molybdenum and tungsten (ref. 1), the fluxionality of (η^6-cycloheptatrienyl) $Mo(CO)_3$ (ref. 2), the area of substituted cyclopentadienyl rings and their synthesis (ref. 3), interpretation of potential constants and application to study of bonding forces in metal cyanide complexes and metal carbonyls (ref. 4).

SYNTHESIS AND REACTIVITY

Metal Carbonyls

The elusive formyl ligand was produced in situ via reaction of $K^+HB(O\text{-}i\text{-}Pr)_3^-$ with $Cr(CO)_6$ yielding $Cr(CO)_5C(O)H^-$ (ref. 5). Its proton magnetic resonance is at 15.25, similar to that of the well-characterized $(CO)_4FeC(O)H^-$ anion. NMR evidence for formyls of $W(CO)_6$, $(CO)_5CrPPh_3$, and $(CO)_5WPPh_3$, similarly produced by reaction with trialkoxyborohydries, was also reported (ref. 5). Several metal carbonyl derivatives of nucleic acid bases and nucleosides such as purine, adenine, adenosine, xanthine, etc., were prepared and characterized (ref. 6). Thus $W(CO)_5L$, $W(CO)_5L^-$, and $Mo(CO)_3enL^-$ were prepared by the photolysis of $W(CO)_6$ in THF/ROH or thermolysis of $Mo(CO)_4en$ in ROH in the presence of L or L^-. The anionic complex $W(CO)_5(2\text{-thiouracilate})^-$ was also produced by base hydrolysis of the neutral $W(CO)_5$(2-thiouracil) (ref. 6). Flash photolysis of $W(CO)_6$ has been reported to result in the production of $W(CO)_5$ (λ_{max} 414 nm) and CO in a one-step reaction (ref. 7). In cyclohexane a rather slow thermal reaction is observed resulting in formation of the original $W(CO)_6$ (k_2 = 89 $M^{-1}sec^{-1}$), whereas in CCl_4 a more rapid process led to the production of $W(CO)_5Cl$ (λ_{max} 385 nm) with a rate constant k_1 = 232 sec^{-1}. In the mixed solvent (CCl_4/C_6H_{12}) formation of $W(CO)_5Cl$ was the predominant process. Results of this study have been interpreted with regard to the rate of metathesis of olefins (ref. 7). The interactions of transition metal carbonyls, $Mo(CO)_6$, $Re_2(CO)_{10}$, and $Ru_3(CO)_{12}$ with a hydrogen γ zeolite were studied by X-ray diffraction, IR and U.V. spectroscopy and volumetric measurements (ref. 8). Complexes were located in zeolite cages. Heating produced progressive CO loss resulting in partially decomposed complexes bound to the framework (ref. 8). on complete decomposition, metal particles retained in zeolite were examined (ref. 8). Photochemical studies of ligand substitution reaction of $W(CO)_5X$ (X=substituted pyridines) show that the W → X charge transfer state is less reactive towards dissociative loss of X than is the lowest ligand field state (ref. 9). Complexes of the form $R_2Sn{:}M(CO)_5$ (R = C_5H_5, M = Cr, Mo, W; R = MeC_5H_4, M = Cr, W) have been prepared by the addition of dicyclopentadienyltin or bis(methylcyclopentadienyl)tin to THF solutions of $M(CO)_5THF$ (ref. 10). A dramatic lowering of the tin-119 Mössbauer isomer shift from 3.74-3.83 mm s^{-1} in the free stannylene ligands to 1.86-2.00 mm s^{-1} in the complexes with a concomitant increase in the quadrupole splitting from 0.8 mm s^{-1} to 2.51-3.13 mm s^{-1} have been interpreted as demonstrating the presence of synergic tin → metal σ - and metal → tin (d → p) π - binding along the tin-metal axis (ref. 10). Substituent effects on the reaction of $Cr(CO)_5C(X)C_6H_4Y$ and SiR_3H in the presence of pyridine to yield $Cr(CO)_5py$ and $SiR_3(C(X)(H)(C_6H_4Y))$, as well as detailed kinetic studies, support the proposed mechanism of a minor first-order dissociative contribution in which the silicon hydride reacts as a nucleophile at the carbene carbon. This work was extended to reactions with other IVA hydrides; variation in rate follow the order Si< Ge << Sn (ref. 11,12). Co-condensation of Cr atoms and N_2 or N_2/Ar has afforded $Cr(N_2)_x$ where x = 1-6, which have been identified by IR/Vis-UV spectra (ref. 13). Side-on di-nitrogen bonding was proposed as a possible explanation for the "anomalous behavior" of the lower coordinated complexes, $Cr(N_2)_2$, x = 1-4 (ref. 13) Verifying earlier electrochemical studies, one- and two-electron oxidations of $Cr(CNR)_6$(R = aryl) by $AgPF_6$ yielded $Cr(CNR)_6^+PF_6^-$ and $(Cr(CNR)_6)(PF_6)_2$ (ref. 14). These sub-18-electron species (μ = 2.0 and 3.0 BM, respectively) appear to be thermally and air stable in the solid state (ref. 14).

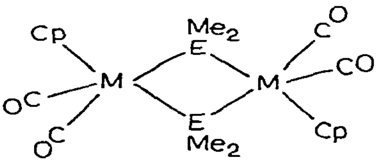
In an attempt to prepared mixed metal carboxylates such as $MM'(O_2CR)_4$, $W(CO)_6$, $Cr(CO)_6$ and pivalic acid were reacted in refluxing o-dichlorobenzene (ref. 15). A compound of stoicheiometry $W_3Cr_3O_{28}C_{65}H_{110}$, containing a triangular W_3 cluster with edge-bridging oxo atoms connecting the W_3 cluster to Cr octahedra, and face bridging alkoxo groups were verified by X-ray crystallography (ref. 15). In the presence of trifluoromethylsulfonic acid, $Mo(CO)_6$ and acetic acid, reagents used to produce $Mo_2(OAc)_4$, react to yield a trinuclear complex salt $(Mo_3(OAc)_6(CH_3CH_2O)_2\ (H_2O_3)^{2+}\text{-}(CF_3SO_3)_2^-$ (ref. 16). Chromium hexacarbonyl reacts with tetrachloro-1,2-benzoquinone to yield $Cr(O_2C_6Cl_4)_3$, whose crystal structure was reported (ref. 17). From the photochemical reactions of $M(CO)_6$ (M = Cr, Mo, W) and $(CH_3)_2\underset{\overset{\|}{O}}{S}-CH_2$ in ether, yellow solids with the composition $((CH_3)_2\underset{\overset{\|}{O}}{S}-CH_2)M(CO)_4$ were obtained in good yields (ref. 18). The isocyanides Me_3MCH_2NC, where M = Si, Ge, Sn and Pb, were prepared via the lithio species $Li(CH_2NC)$ and MeMX (ref. 19). These were then reacted with $Mo(CO)_6$ to form complexes: $Mo(CO)_{6-x}(CNCH_2MMe_3)_x$ (x = 1,2, and 3) and with $Cr(CO)_6$ to form $Cr(CO)_5\text{-}CNCH_2MMe_3$. IR data were recorded and shifts of ν(CN) and ν(CO) were interpreted in terms of the inductive effect of the Me_3M-group (ref. 19). The halogen bridged molybdenum and tungsten dimeric carbonyl derivatives have been prepared via reaction 1, where alkyl=ethyl and methyl, by Hohmann and tomDieck (ref. 20).


(1)

The thiocarbonyl complexes $M(CO)_5CS$(M=Cr, Mo, W) were prepared by reaction of Na/Hg-reduced $M(CO)_6$ (presumably $M_2(CO)_{10}^{-2}$) with thiophosgene, Cl_2CS (ref. 21). A most convenient chemical separation of $W(CO)_5CS$ from $W(CO)_6$ illustrates the major difference in the CS and CO ligands. That is, under mild conditions such that $W(CO)_6$ is unreactive, $n\text{-}Bu_4N^+I^-$ readily reacts with $W(CO)_5CS$ forming $n\text{-}Bu_4N^+W(CO)_5CS^-$ by reaction with Ag^+ in the presence of CO. Extensive ligand substitution reactions confirm the inertness of CS to substitution, and the ability of CS to labilize CO (ref. 21). A series of reactions of tungsten thiocarbonyl complexes with electrophiles was reported (ref. 22). For example, CF_3SO_3H protonated $W(CO)(CS)(diphos)_3$ yielding $(HW(CO)(CS)(diphos)_2)CF_3SO_3$; whereas other Lewis acids add to the thiocarbonyl sulfur. Products such as $W(CO)_4(I)CSR$ were formed via alkylation of $Bu_4N(W(CO)_4(CS)I)$ by $MeOSO_2F$ and $Et_3O^+BF_4^-$. Nucleophiles such as NH_2R, NHR_2', and N_3^- react with the less electron rich thiocarbonyl, $W(CO)_5CS$, forming adducts in which the donor atom binds to the thiocarbonyl carbon, ultimately yielding $W(CO)_5CNR$, $W(CO)_5(S{=}C(H)NR'_2)$, and

$W(CO)_5NCS^-$, respectively (ref. 23). The stereospecific synthesis of trans-$W(CO)_4(^{13}CO)CS$ may be effected in high yield through reaction of Bu_4N(trans-$W(CO)_4(CS)I$) with $AgBF_4$ or $AgCF_3SO_3$ in the presence of ^{13}CO (25 psi) (ref. 24). The silver salt technique was also used to prepare cis-$W(CO)_4(^{13}CO)L$ ($L = CNC_6H_{11}$, $P(4\text{-}ClC_6H_4)_3$) from cis-$W(CO)_4(L)Cl^-$. Studies of intramolecular isomerization of trans-$W(CO)_4(^{13}CO)CS$ and of CO dissociation are included in this report (ref. 24). The X-ray structural data of trans-$W(CO)_4(CNC_6H_{11})(CS)$ have shown that the W-C bond lengths of the three isoelectronic ligands increase in the order: W-CS(1.944Å) < W-CO(2.0645Å, ave.) < W-CNC_6H_{11}(2.158Å) (ref. 25). Using data from this and other thiocarbonyl derivatives an excellent correlation was observed between the C-S distances and the CS stretching frequencies (ref. 25). The behavior of $M(CO)_5CS$ (M = Cr or W) towards UV photolysis in an Ar or CH_4 matrix is to produce two isomeric forms of $M(CO)_4CS$ (ref. 26). Based on interpretation of the IR of ^{13}CO labelled molecules the two structures are proposed to be square pyramidal C_{4v} (CS at apex) and square pyramidal C_s (CS in basal plane) (ref. 26). Stereospecifically labelled trans-$W(CO)_4(^{13}CO)(CS)$ was also used to determine that the photolytic loss of CO from the axial or equatorial position with respect to the thiocarbonyl is equally probable (ref. 27). Importantly, rearrangement occurs after loss of CO, in an excited state, and this leads to the observed geometrical distribution of C_{4v} and C_s $W(CO)_4(CS)$ fragments (ref. 27).

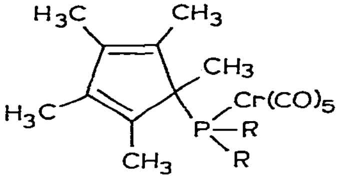
Novel derivatives of $M(CO)_6$ included the synthesis of $(CpFe(CO)_2)_3Sb \rightarrow M(CO)_5$ (M = Cr, W) (ref. 28). The ferrio-stibane ligand was prepared by reaction of $SbBr_3$ or SbF_3 with $Na^+CpFe(CO)_2^-$ (ref. 28). Similar metal-bridging stibane derivatives such as $((Cp)(CO)_2Fe)R_2Sb \rightarrow M(CO)_5$ (R = Me or Br; M = Cr, W), $((Cp)(CO)_2Fe)_2BrSb \rightarrow M(CO)_5$, and $((Cp)(CO)_3Mo)R_2Sb \rightarrow Mn(CO)_2Cp$ (R = Me or Br) were also reported (ref. 29). The similarly stibane-bridged complexes $(Cp(CO)_3M')Br_2Sb - M(CO)_5$(M and M = Cr, W) could be converted to difluoro derivatives by treatment with $AgBF_4$ (ref. 30). Continuing this work, $Cp(CO)_3W\text{-}AsMe_2$ and $(Cp(CO)_3W)_2SbMe$ were found to react with $Ni(CO)_4$ under mild conditions to give $L \rightarrow Ni(CO)_3$ products (ref. 31). At higher temperatures both products could be further reacted with L, splitting out CO as $Ni(CO)_4$ and yielding 4-membered metallo-Va-cycles, for example, I (ref. 31).



E = As, Sb
M = Mo, W

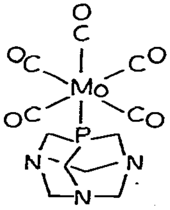
I

Synthesis of μ-(tetraphenyldiphosphine)decacarbonyldimolybdenum, $(CO)_5MoPPh_2$-$PPh_2Mo(CO)_5$(I) has been achieved by treatment of $(CO)_5MoPPh_2Cl$ with ethylmagnesium bromide (ref. 32). The $(CO)_5$Cr-bound ligand PMe_2SH can be methylated with diazomethane to yield $Cr(CO)_5PMe_2SMe$ (ref. 33). In addition, Na reduction of $Cr(CO)_5PMe_2SH$ yields the anion $Cr(CO)_5PMe_2S^-$ which in the presence of $Cr(CO)_5$THF can be used to link two Cr centers thus preparing $((OC)_5Cr \leftarrow PMe_2S - Cr(CO)_5)^-$ (ref. 33). Other ligand bridging complexes recently synthesized were $(CO)_5Cr$-PMe_2PMe_2-M where M=$Mn(CO)_2Cp$, $Fe(CO)_4$, Co(CO)Cp, $Ni(CO)_3$, etc. (ref. 34). Photolysis of $(CO)_5Cr$-PMe_2PMe_2 yielded the dimetallocycle $(CO)_4Cr(PMe_2$-$PMe_2)_2Cr(CO)_4$ (ref. 34). The synthesis and ^{31}P NMR spectra of a series of pentamethylcyclopentadienylphosphanes (II) have been reported by Jutzi and coworkers (ref. 35).



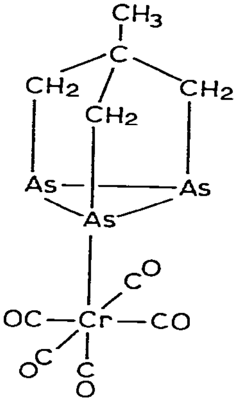
II

Comparison of crystallographic and spectral characterizations of $Mo(CO)_5(P$-$(CH_2)_6N_3)$, III, suggested the ligand to be of σ-donating capability similar to PPh_3 and of steric properties similar to PMe_3 (ref. 36).



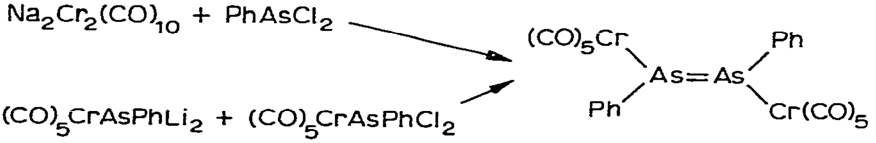
III

Novel pentacarbonyl derivatives of the type $M(CO)_5P(t\text{-}Bu)_2EMe_2Cl$ (M = Cr, Mo, W; E = Ge, Sn) were prepared and their spectral properties recorded (ref. 37). The reaction of RR'_2 with Me_3SnCH_2I initially gave quaternary phosphonium cations $(RR'_2PCH_2SnMe_3)^+$(R = $(CO)_5MPPh_2CH_2CH_2$, M=W, Mo, R'=Ph; R=R'=Ph; RMe, R'=Ph; RPh, R'=Me), which were unstable in $HCCl_3$ and MeOH but stable in Me_2SO (ref. 38). Derivatives of $M(CO)_6$, monosubstituted with the cage compound P_4O_6, were prepared and the mass spectra, ^{31}P NMR and ν (CO) IR spectra recorded (ref. 39). The $CH_3C(CH_2As)_3Cr(CO)_5$ derivative (IV) has been synthesized from the corresponding cyclic triarsane and $Cr(CO)_6$ in THF under photolysis (ref. 40).



IV

Two routes which lead to the Ph_2As_2 bridged complex V are shown in the following diagram (ref. 41)



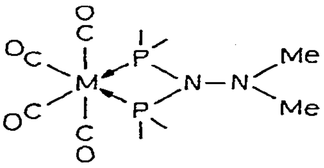
V

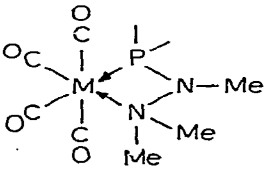
(2)

Schenk has reported the preparation of substituted carbonyl metallates of the type $[LM(CO)_4X]^-$)L = phosphine, phosphite, M = Mo, W, X = Cl, Br) by thermal or photochemical CO-displacement from the parent pentacarbonyl metallate. These new derivatives were isolated as the tetraethylammonium salts and characterized by their infrared spectra in the ν(CO) region in tetrahydrofuran solution (ref. 42) Trifluoroacetic acid has been shown to protonate the series of metal carbonyl derivatives $M(CO)_{6-n}(PA_3)_n$ (M = Mo W, A=CH_3, OCH_3; n=3, 4). Infrared and proton NMR studies demonstrate stereochemical non-rigidity in these $[HM(CO)_{6-n}(PA_3)_n]^+$ heptacoordinated cationic species (ref. 43). The reaction of trans-$Mo(N_2)_2(dppe)_2$ with DMF gives the carbonyl complex, Mo(CO)(DMF)(dppe)$_2$, which reacts readily.with N_2 gas to form the dinitrogen complex, trans-

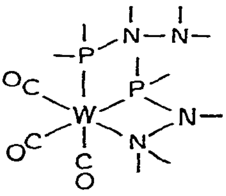
$Mo(CO)(N_2)(dppe)_2$; the dinitrogen ligand is so labile as to be displaced to afford the complexes, $[Mo(CO)(dppe)_2]_n$ and $Mo(CO)L(dppe)_2$(L = donor compounds) (ref. 44). Complexes of aromatic or α,β-unsaturated nitriles R'CN of the type $(R'CN)_2(PR_3)_2Mo(CO)_2$ and $(R'CN)(PR_3)_3Mo(CO)_2$ are new chromophores (ref. 45). Their intense electronic absorption band in the visible spectrum is strongly influenced by substituents and solvent polarity (ref. 45).

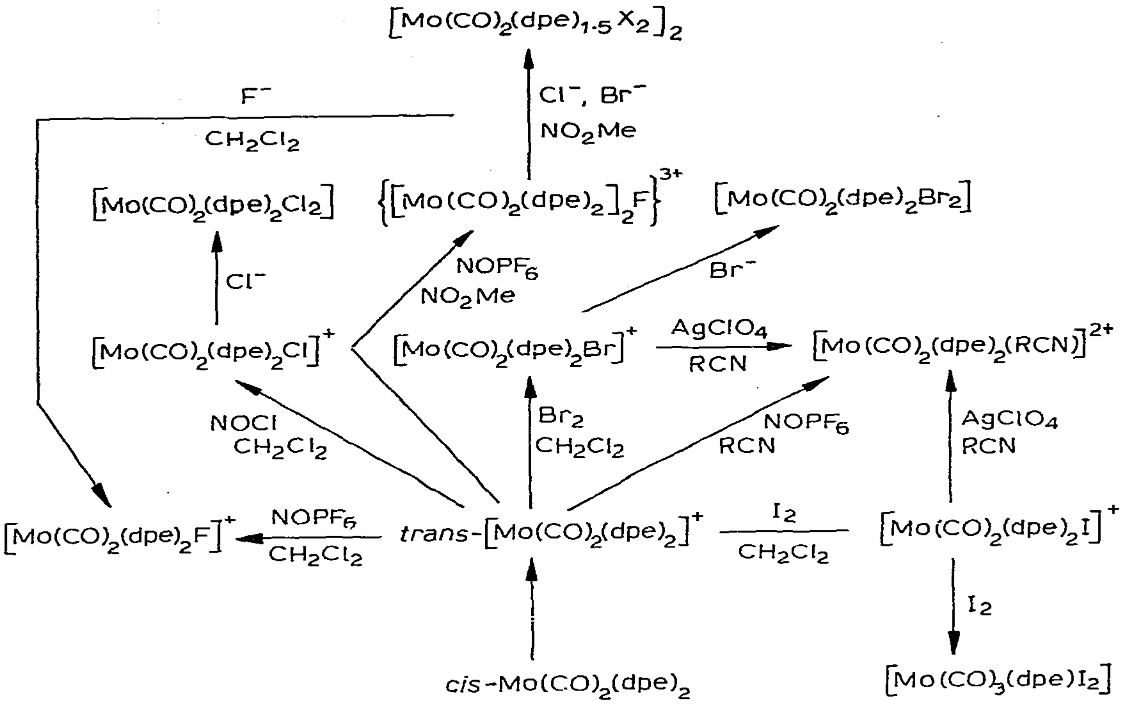
Derivatives such as $(L\text{-}L)M(CO)_4$(M = Cr, Mo, W) and $(L\text{-}L)M(CO)_3Br_2$ (M = Mo, W) where L-L is the very bulky, sterically shielding neopentyldiphosphine ligand, $(Me_3CCH_2)_2PCH_2CH_2P(CH_2CMe_3)_2$ were prepared by the thermal displacement of CO from $M(CO)_6$ and via bromination of $(L\text{-}L)M(CO)_4$ respectively (ref. 46). A triligating ligand, $(Me_3CCH_2)P[CH_2CH_2P(CH_2CMe_3)_2]_3$ formed facial derivatives of $Mo(CO)_3$ and $Cr(CO)_3$ when the ligand was reacted with (cycloheptatrienyl)$M(CO)_3$ (ref. 46). Monodentate N-diphenylphosphinohydrazine derivatives, $LM(CO)_5$, $L_2M(CO)_4$ and $L_3M(CO)_3$, are all phosphorus bound (ref. 47). The chelate complexes VI, VII, and VIII could be readily prepared by either thermal substitution of CO, or by a labile ligand technique; however the authors were unable to prepare binuclear, phosphinohydrazine bridging complexes (ref. 47).


VI


VII

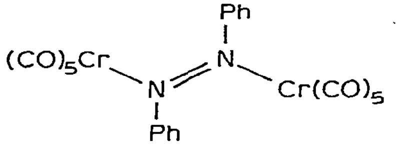
Various oxidation reactions of $Mo(CO)_2(dppe)_2$, with $NOPF_6$, NOCl, Br_2 and I_2 were examined and analyzed by conductance, IR and NMR (^{31}P and ^{19}F) (ref. 48). Low temperature ^{31}P NMR showed that $[Mo(CO)_2(dppe)_2F]^+$ is a rigid system while $[Mo(CO)_2(dppe)_2Br]^+$ and $[Mo(CO)_2(dppe)_2I]^+$ are fluxional (ref. 48).


VIII



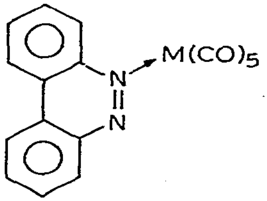
Reaction of Ph_2PCl with NH_2CHRCO_2Me (R=H, iso-Pr) affords stable bidentate aminophosphines, $(Ph_2P)_2NCHRCO_2Me$; transition metal complexes (optically active for R=iso-Pr) are reported for Mo(0) (ref. 49).

Whereas *cis*-azobenzene reacts with $Cr(CO)_5 \cdot THF$ to yield the nitrogen-lone pair ligated, mononuclear complex $(PhNNPh){-}Cr(CO)_5$, *trans*-azobenzene reacts with the $THF \cdot Cr(CO)_5$ complex, *not in solution but during the course of drying the residue*, to yield the dinuclear species, IX (ref. 50). Thermal reaction of these reagents in diglyme leads to π-arene complexes (ref. 50).

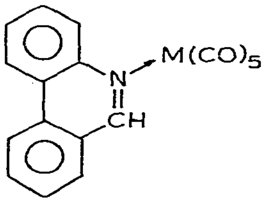


IX

The reactions of aminetungsten pentacarbonyls and bis(amine)-tungsten tetracarbonyls with bromine or iodine to provide $W(CO)_4(amine)X_2$ and $W(CO)_3{-}(amine)_2{-}X_2$ derivatives have been described (ref. 51). The iodide compounds are more stable than their chlorine analogs. The complexes were shown to be nonelectrolytes in benzene solution by conductivity measurements (ref. 51). The reaction of $M(CO)_5NCCH_3$ (M = Cr, Mo, W) with sodium bis(trimethylsilyl) amide does not lead to the transformation of a CO group into CN^-, but instead, to a deprotonation to give the anions $[M(CO)_5NCCH_2]^-$ (ref. 52). Both mononuclear $Cr(CO)_5$-$(C_2N_2N_4)$ and binuclear $[Cr(CO)_5]_2(C_2H_2N_4)$ are formed when s-tetrazine $(C_2H_2N_4)$ is added to a photolysed solution of $Cr(CO)_6$ in diethyl ether (ref. 53). A centrosymmetric structure is proposed for the binuclear, s-tetrazine-bridged complex $[Cr(CO)_5]_2(C_2H_2N_4)$ (ref. 53). The corresponding molybdenum and tungsten compounds are also described (ref. 53). Complexes of the type $M(CO)_5L$ (L=benzo, cinnoline and phenanthridine; M=Cr, Mo, W) (X,XI) have been prepared (ref. 54). Bonding through the nitrogen base has been established by ^1H and ^{13}C NMR studies (ref. 54).



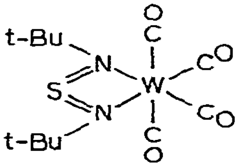
X



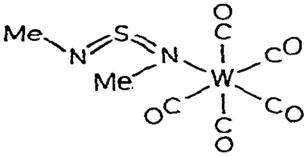
XI

Alkylation of $M(CO)_5NCX^-$ by R_3O^+ or $ROSO_2F$ has yielded some twenty neutral cyanates, thiocyanates, and selenocyanates of Cr and W, all N-bound (ref. 55). No RXCN derivatives of Mo nor R-NCX derivatives of any VIB metal could be ioslated (ref. 55). Sellmann, et. al., have reported the synthesis, properties and reactions of $[(CO)_5Cr]_2N_2H_4$, $(CO)_5CrN_2H_4$ and $(CO)_5CrNH_3]$, as well as attempts to prepare $[(CO)_5Cr]_2N_2$ and $(CO)_5CrN_2$ (ref. 56).

Vrieze and co-workers have reported the preparation and properties of $M(CO)_4(RN{=}S{=}NR)$(M=Cr, Mo, W; R=i-Pr,t-Bu) (XII) and $M(CO)_5(RN{=}S{=}NR)$ (M=Cr, W; R=Et, i-Pr) (XIII) (ref. 57). The pentacarbonyl derivatives were shown to be fluxional; attributed to a gliding movement of the metal atom along the N=S=N system (ref. 57).

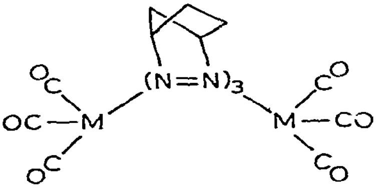


XII



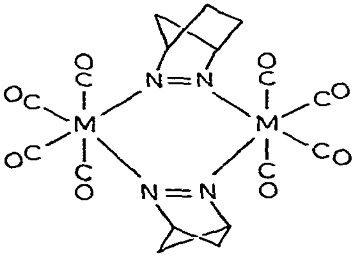
XIII

Binuclear complexes containing 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) (XIV and XV) are very readily formed (ref. 58). For M = Mo, the cis-Mo(CO)$_4$(DBH) complex spontaneously converts to XIV at room temperature even in the presence of excess DBH (ref. 58).

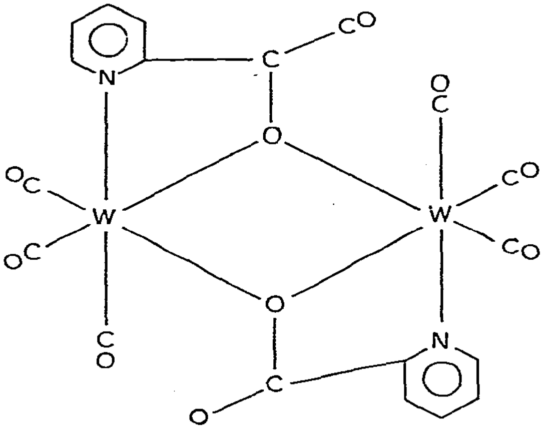


XIV

Reflux of pyridine-2-carboxylic acid (picH) with M(CO)$_6$ in MeOH afforded H_2, CO, and [Cr(pic)$_3$], [Mo(pic)$_3$]·MeOH and W(pic)$_4$ (ref. 59). A mixed carbonyl-pic derivative whose structure was proposed to be that of a dinuclear complex, XVI was obtained in the stoiochiometric reaction of W(CO)$_6$ and picH (ref. 59).



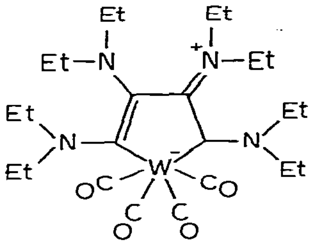
XV



XVI

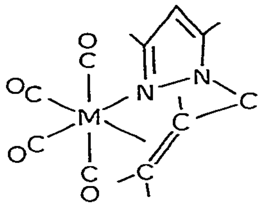
XVI

The reactions of the W(I) complex of picolinic acid (Hpic), $[W(CO)_3(pic)]_n$, with certain monodentate tertiary phosphines affords a convenient route to complexes of the type $W(CO)_3(PR_3)_3$ and $HW(CO)_2(PR_3)_2(pic)$. The latter hydrido complexes of W(II) were characterized by IR and NMR spectroscopy (ref. 60). The synthesis of many transition metal carbonyl derivatives of aminoalkynes included that of $(Et_2N)_4C_4W(CO)_4$, prepared by photolysis of $W(CO)_6$ and $Et_2NC \equiv CNEt_2$, whose possible structure is XVII (ref. 61).



XVII

Photochemical reaction of 1-allyl-3,5-dimethylpyrazole with $M(CO)_6$(M= Cr, Mo, W) has afforded novel mono-olefin derivatives in which both pyrazolyl-N and the olefinic portion of the allyl group are coordinated to the metal in the <u>cis</u>-configuration (XVIII) (ref. 62). The ligand N-allylpyrazole bound to chromium- and molybdenum-tetracarbonyl was found to be easily displaced by other donor ligands such as tertiary phosphines or phosphites (ref. 62).



XVIII

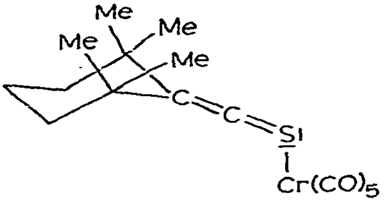
Isolation and characterization by I.R., UV-visible and ^{1}H NMR of the following types of complexes were reported (ref. 63).

1\. $[\{M(CO)_5\}_2L]$ a. M = Cr, W
L = $RS(CH_2)_nSR$
1\. R = Me and n = 6
2\. R = Et and n = 2 or 4
b. M = W
R = Me or t-Bu; n = 2

2\. $[M(CO)_5L]$ a. M = Cr or W
L = $MeSCH_2Ph$
b. M = Cr
L = $EtS(CH_2)_2SEt$

3\. $[M(CO)_4L]$ M = Cr, Mo or W
L = $EtS(CH_2)_2SEt$

Bonding of the alkyl sulphide to group 6 metal carbonyls is discussed. The bridged ligand complexes of n = 2 decompose affording the related chelate complex and the parent hexacarbonyl (ref. 63). Phosphine sulfide metal complexes $M(CO)_5S{:}PHR_2$ (R = Me, Et, Ph; M = Cr, Mo, W) were prepared by the indirect photochemical reaction of $M(CO)_5(THF)$ with $R_2HP{:}S$ (ref. 64). These complexes undergo intramolecular rearrangements under mild conditions to give $(CO)_5MPR_2SH$ (ref. 64). Band-shape fitting studies for the NMR spectra of the benzylic methylene protons of $M(CO)_4L[M = Cr, Mo, W; L = (PhCH_2SCH_2)_2]$ showed that the coalescence phenomenon observed in the temperature-dependent NMR spectra resulted from inversion of configuration about the ligand S atoms rather than from reversal of the chelate ring (ref. 65). The thioketene complex (XIX) has been synthesized from $Cr(CO)_6$ and the stable alkyl thioketene, 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane in tetrahydrofuran solvent (ref. 66).



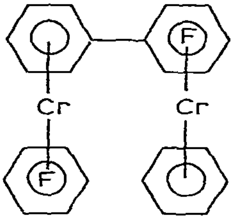
XIX

Yellow complexes of the composition $(CH_3)_2S(=O)CH_2M(CO)_5$ have been obtained from the reaction of $(THF)M(CO)_5$ (M=Cr, Mo, W) with $(CH_3)_2S(=O)CH_2$ in tetrahydrofuran. Their infrared and proton NMR properties were described (ref. 67). The hitherto unreported complex, $W(CO)_5SH_2$ was prepared via photolysis of $W(CO)_6$ in the presence of H_2S gas in pentane (ref. 68). Lustrous green crystals, sublimable with partial decomposition, were obtained and characterized (ref. 68).

Several heptacoordinate VIb carbonyl-halides and isocyanide complexes were described according to their structural deviation from idealized symmetries of D_{5h}, C_{3v} and C_{2v} (ref. 69). $[M(CO)_2(NO)(\text{o-phen or -bipy})]_2$ (M = Mo, W) derivatives have resulted from the reaction of a benzene solution of $M(CO)_4(\text{o-phen or -bipy})$ with a slow stream of NO (ref. 70). Under similar conditions $M(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ (M = Cr, Mo) gave $M(NO)_3(Ph_2PCH_2CH_2AsPh_2)$, whereas $W(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ afforded the nitrosyl carbonyl complex $W(CO)(NO)_2(Ph_2PCH_2CH_2AsPh_2)$ (ref. 70). A study of halogen oxidation of some amine chromium and amine molybdenum carbonyls was reported (ref. 71). Isolated species include (ref. 71), $Cr(CO)_3(\text{amine})X_2$, $Mo(CO)_4(\text{amine})X_2$, $Mo(CO)_3(\text{amine})_2X_2$, $Mo(CO)_2(\text{amine})_2X_2$, and $[Mo(CO)_3(\text{amine})_3X]X$.

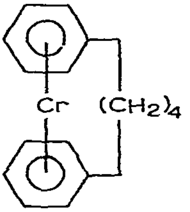
Aromatics and Cyclopentadienyls

Aromatics. Bis(2,6-dimethylpyridine)chromium was prepared by the co-condensation method (ref. 72). Two crystal modifications were analyzed by x-ray crystallography and both show the 2,6-dimethylpyridine units to be parallel but staggered relative to each other (ref. 73). Substituted bis(arene)chromium complexes were prepared by reacting $(C_6H_6)Cr(C_6F_5H)$ synthesized by the metal atom/vapor co-condensation technique with n-BuLi and converting the lithiated complex to $(C_6H_6)Cr(C_6F_5X)$ (X = $SiMe_3$, Co_2Li, CMe_2OH, $CpFe(CO)_2$, etc.) (ref. 74). Several compounds in which π-sandwich organometallics, such as dibenzenechromium or -molybdenum, cyclopentadienyl-cycloheptatrienylchromium, etc., have been intercalated into crystalline ZrS_2 were reported (ref. 75). The stoichiometry of the compounds is 1/6 bis-arene "guest molecules" per ZrS_2 unit and 1/4 metallocene "guests" per ZrS_2 (ref. 75). Noteworthy is that successful intercalates occur with those sandwich complexes whose ionization potentials are low, < 6.2 eV (ref. 75). The reactions of $[CpMo(\eta^6\text{-}C_6H_5Cl)]$ with ligands such as 1,2-bis(diphenylphosphino)ethane (dppe), CH_3CN, COT, etc., have been explored (ref. 76). Several non-carbonyl containing products were observed and the x-ray crystal structure of one of them, $[(Cp)Mo(dppe)(\eta^4\text{-}C_6H_8)][PF_6]$, was reported (ref. 76). Ring poly-substituted products were obtained on reacting fluorinated bis(arene)chromium complexes such as $(\eta^6\text{-}C_6H_5F)_2Cr$ and $(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6F_6)Cr$ with the nucleophiles NaOMe, n-BuLi, PhLi, and t-BuLi (ref. 77). Tertiary butyllithium is also capable of proton abstraction from $(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6F_6)Cr$ yielding the condensed product (XX) (ref. 77).

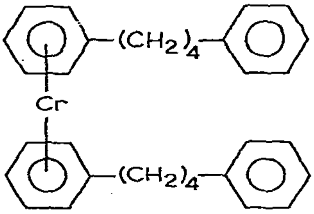


XX

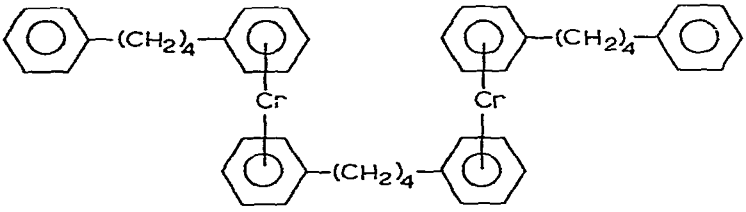
Bridged dibenzenechromium complexes (XXI, XXII and XXIII) were prepared in 6, 29, and 15% yields, respectively, from the reaction of 1,4-diphenylbutane with Cr vapor (ref. 78).



XXI



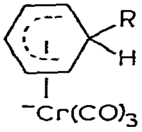
XXII



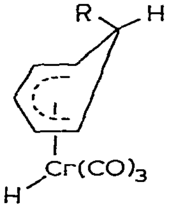
XXIII

In comparison with $(C_6H_6)Cr(CO)_3$, $(C_6H_6)_2Cr$ is relatively light stable (ref. 79). The major part of the light energy absorbed by $(C_6H_6)_2Cr$ leads neither to its decomposition nor ligand exchange, nor can it be transferred to common low energy triplet acceptors. Internal dissipation of energy, either by rapid conversion to the ground state or by rapid reversible isomerization, must be an important process (ref. 79).

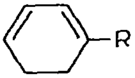
Studies on reactions of the carbanion addition product (XXIV) with weak acids led Semmelhack and coauthors to propose a metal-protonated intermediate, (XXV), which subsequently decomposes to the neutral precursor of XXIV, $C_6H_6Cr(CO)_3$, and RH. Strong acids, however, protonate the cyclohexadienyl ligand to yield the diene (XXVI) (ref. 80).



XXIV



XXV

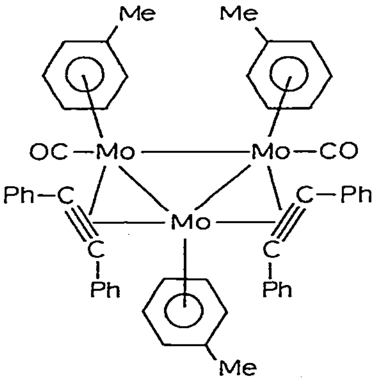


XXVI

In marked contrast to the action of $NO^+PF_6^-$ on (arene)$Cr(CO)_3$ yielding (arene)-$Cr(CO)_2NO^+PF_6^-$, reactive fragments formulated as $CrCl(CO)(CO)_2$ are apparently formed using NOCl as nitrosylating reagent (ref. 81). Addition of CpNa, indenyllithium and fluorenyllithium to this derivative yields $CpCr(CO)_2NO$, (η^5-indenyl)-$Cr(CO)_2NO$ and (η^5-fluorenyl)$Cr(CO)_2NO$, respectively (ref. 81). The molecular structure of (1'-t-butyl-2',2'-dimethylpropyl)-π-(tricarbonylchromium)benzene has been reported and the temperature dependence of its ^1H NMR spectrum studied over the temperature range 0-115°C (ref. 82,83). Two conformers were detected, where the conformational isomerism is caused by a restricted rotation about the bond between the alkyl group and the complexed aromatic ring (XXVII). The free energy of activation ($\Delta G^{\neq}$) for the interconversion was determined to be 16.9 kcal-mol^{-1} (ref. 82,83).

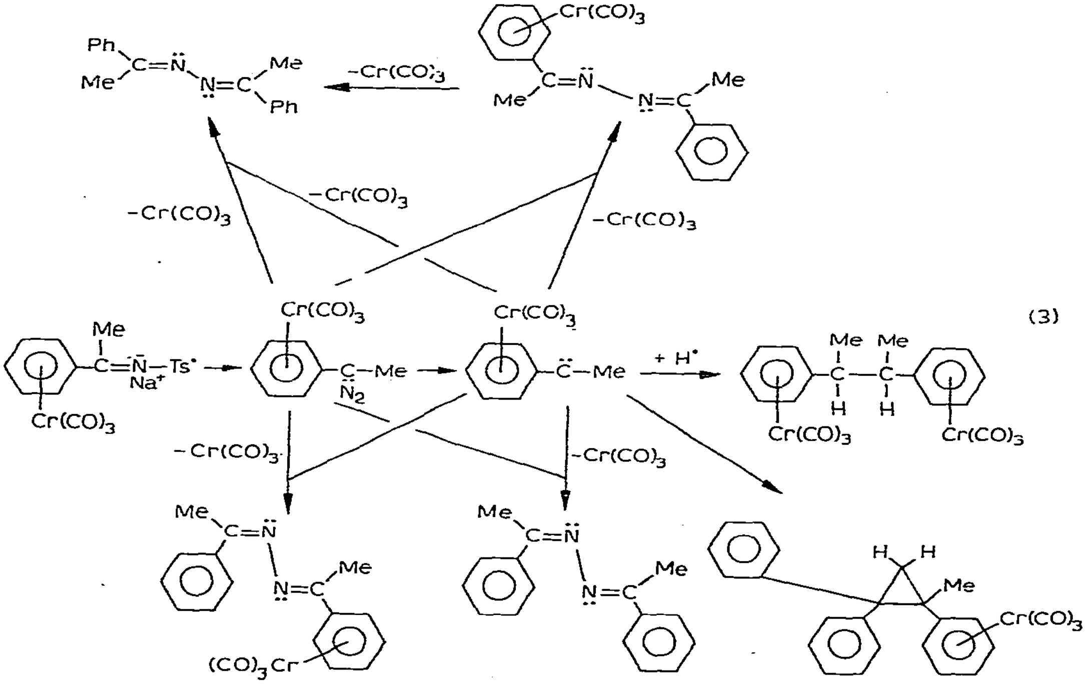
XXVII

The metal-bound SMe_2 ligand in $(C_6H_6)Cr(CO)_2SMe_2$ and Cp-manganese analogues can be reversibly S alkylated, yielding metal-bound sulfonium cation derivatives, i.e., $C_6H_6Cr(CO)_2SMe_3^+$ (ref. 84). The IR wavenumbers and half-band width's of the carbonyl stretching vibrations of several substituted η^6-(tricarbonylchromium)benzenes in isoctane solution are reported (ref. 85). Only small perturbations of C_{3v} symmetry are observed (ref. 85). The effect of coordination of $C_6H_5SiMe_xCl_{3-x}$ (x=0-3) to $Cr(CO)_3$ is to increase reactivity of the aryl silane towards phenyl-silicon bond cleavage by HCl, thus producing $C_6H_6Cr(CO)_3$ and $SiMe_xCl_{4-x}$ (ref. 86). The dependence of reactivity on pressure changes (5-4000 atm) was discussed in terms of mechanistic possibilities (ref. 86). Reaction of toluenetricarbonylmolybdenum with diphenylacetylene led to four products: 1. A red complex gave properties identical to bis(pentaphenylcyclopentadienyl)molybdenum, 2. A purple complex gave properties identical with tetraphenylcyclobutadienebis (diphenylacetylene)carbonylmolybdenum, $(Ph_4C_4)(Ph_2C_2)_2MoCO$, 3. A yellow compound tentatively assigned as hexaphenyldewarbenzene and 4. The green compound's analysis is as shown below (XXVIII): (ref. 87)



XXVIII

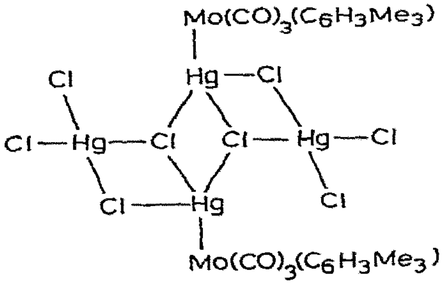
When warmed to room temperature in an atmosphere of CO the co-condensation products of Cr atoms and styrene at -196°C in a pentane matrix were (η^6-$C_6H_5C_2H_3$)$Cr(CO)_3$ and polystyrene derivatives $(C_8H_8)_nH_2Cr(CO)_3$(n=3-7) (ref. 88). Pyridine η-complexes are prepared by treating 2,6-dimethylpyridine and 2,3,5,6-tetramethylpyridine with $Cr(CO)_6$ (ref. 89). Thus, tricarbonyl(2,6-dimethylpyridine)chromium(0) and tricarbonyl(2,3,5,6-tetramethylpyridine)chromium(0) are obtained (ref. 89). IR and ^{1}H NMR spectra are discussed together with those of tricarbonyl(pentamethylpyridine)chromium(0) and tricarbonyl(2,4,6-trimethylpyridine)chromium(0) (ref. 89). Bly and co-workers have prepared the substituted benzyl tosylates, p-phenyl, p-(η^6-phenylchromiumtricarbonyl), p-(p'-nitrophenyl), m-phenyl, m-(η^6-phenylchromiumtricarbonyl) and m-(p'-nitrophenyl) and measured their solvolysis rates in buffered and/or unbuffered acetic acid (ref. 90). Their relative reactivities with respect to benzyl tosylate (1.00) were found at 69.0° C to be the following: 10.8, 7.14, 0.742, 0.571, 0.134 and 0.173, respectively (ref. 90). The ability of α-(η-phenylchromiumtricarbonyl) to stabilize electrophilic centers was compared with that of α-ferrocenyl (ref. 90). An examination of the pyrolysis of the sodium salt of tricarbonyl-(acetophenone)chromium(p-tosylhydrazone) in order to generate tricarbonyl-



(3)

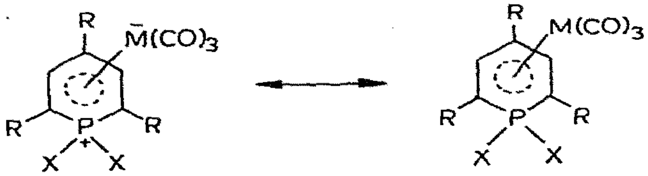
(methylphenylcarbene)chromium was accomplished to study the effect of the tricarbonylchromium group on the spin state of a carbene and stereochemistry of the resulting products (ref. 91).

The crystal and molecular structure of the compound $[(C_6H_3Me_3)(CO)_3Mo(HgCl_2)_2]_2$ (XXIX) was determined from x-ray diffractometer data (ref. 92). The structure consists of centrosymmetric dimers in which the $(C_6H_3Me_3)(CO)_3MoHg_2Cl_2$ ring has one Mo bonded to each Hg (ref. 92). The average upward shift of 58 cm^{-1} in the IR CO stretching frequencies on complex formation is consistent with a bonding model in which formally nonbonding electrons of Mo are donated into empty σ orbitals on Hg (ref. 92).



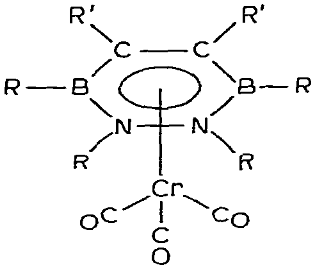
XXIX

Hetero-atom π-complex derivatives of VIb metal tricarbonyls (4) were synthesized by reacting the λ^5-phosphorin with $M(CO)_6$ or $M(CO)_3(CH_3CN)_3$ in dioxane (ref. 93). An x-ray crystal structure determination of the air stable solid derivative of Cr showed the $Cr(CO)_3$ moiety to be skewed away from the P in the still planar ring (ref. 93).



(4)

Yet another heteroatom π-complex (XXX) was prepared by reacting the cyclic $C_2B_2N_2$ derivative with $Cr(CO)_3(CH_3CN)_3$ (ref. 94). Spectroscopic data suggests that the ligand acts as a hexahapto-6-electron donor ligand (ref. 94).



XXX

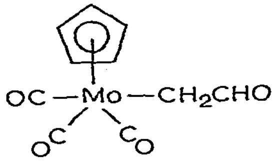
A paramagnetic chromocarborane, $(Et_4N)_2[4,4'\text{-}Cr\text{-}(1,6\text{-}C_2B_{10}H_{12})_2]$, was prepared in a series utilizing the $C_2B_{10}H_{10}R_2^{2-}$ ligand and early transition metals (ref. 95).

Cyclopentadienyls.

The relative basicity of the different sites in a variety of cyclopentadienyl and arene derivatives of group VIB and VIIB transition metal carbonyl and nitrosyl complexes towards Lewis acids in solution has been investigated using infrared spectroscopy (ref. 96). Adduct formation at the metal atom was observed for $CpRe(CO)_2L$ (L=CO, PR_3) with $SnCl_4$, $SnBr_4$, $TiCl_4$; (arene)$M(CO)_3$ (M=Cr, Mo, W) with $SnCl_4$, $TiCl_4$; and $Ph_3PC_5H_4M(CO)_3$ (M=Cr, Mo, W) with $TiCl_4$ and $AlCl_3$. The carbonylnitrosyl complexes $CpM(CO)_2NO$ and $CpM(CO)(NO)PPh_3$ (M=Mo, W) were reported to form adducts, depending on their donor and acceptor nature, involving the oxygen atoms of CO or NO groups or the metal atom (ref. 96). On the other hand, $CpCr(CO)_2Cl$ was reported to react with Lewis acids via the chlorine atom (ref. 96). Similarly, studies of $CpCr(CO)_2Cl$ and $MoCl_2(NO)_2(PMe_3)_2$ with $FeCl_3$ indicate coordination of $FeCl_3$ at the Cr-Cl and Mo-Cl sites (ref. 97). All carbonylmetallate monoanions which are weaker nucleophiles than $CpFe(CO)_2^-$ and $Re(CO)_5^-$, including $CpM(CO)_3^-$ (M=Mo, W) have been shown to be unreactive toward Ph_4As^+ at room temperature (ref. 98). Reduction of isocyanide derivatives of metal carbonyl halides such as $CpMo(CO)_2(CNMe)Cl$, $CpMo(CO)(CNMe)_2Cl$, and $Mn(CO)_{5-x}(CNMe)_xBr$ (x=1-3) with Na/Hg yield the corresponding anions (ref. 99). Typically, such anions react with HgI_2 to yield, for example, $CpMo(CO)_2(CNMe)HgI$ or $[CpMo(CO)_2(CNMe)]_2Hg$, and with IVa halides to yield, for example, $CpMo(CO)_2(CNMe)R$ where R=$GeMe_3$, $SnMe_3$, $PbPh_3$, and CH_2CN (ref. 99). Alkyl halides other than $CH_2(CN)Cl$ reportedly give reaction products complicated by insertion rearrangements (ref. 99). In an additional report of facile reductions of metal carbonyls, the procedure for using the electron carrier system Na/hexamethylphosphorictriamide was described for a number of cyclopentadienyl derivatives including the reductive cleavage of $[CpMo(CO)_3]_2$ yielding $CpMo(CO)_3^-$ (ref. 100). The reaction of PCl_3 and $Na^+[CpM(CO)_3]^-$ (M=Cr, Mo, W) or $CpM(CO)_3SiMe_3$ yielded $CpM(CO)_3PCl_2$ (ref. 101). Addition of S_8 produced $CpM(CO)_3Cl$ formation, whereas substitution of a CO by $PPhMe_2$ destabilized the complex (ref. 101). The photochemical synthesis of CpCr(CO)L(NO), where L=py, CH_3CN, γ-picoline, PPh_3, simple olefins, cycloolefins, π-acid olefins, and alkynes, was reported (ref. 102,103). A binuclear derivative, linked by 1,5-cyclooctadiene, $[CpCr(CO)(NO)]_2C_8H_{12}$ was also prepared (ref. 103). Inglis and Kilner were unable to insert carbon monoxide into the M-N bond of complexes such as $CpM(CO)_2X$ ($X=N-CR_2$ or N(R)R'), but rather $[CpM(CO)_3]_2$ or $M(CO)_6$ were the observed carbonylation products (ref. 104). Reactions of acetylenes with the perfluorothiolates $CpM(CO)_3SR_F$ proceed with CO loss to give the formally electron-deficient $CpM(CO)(RC_2R)SR_F$ (M=Mo or W; R=Me, CF_3, Ph; $R_F=CF_3$, C_6F_5) (ref. 105). The reaction of $CpMo(CO)_3Cl$ with $SFO_2(OMe)$ proceeded with chloride abstraction; with the same alkylating agent $K_3[Cr(CN)_5NO]$ was methylated yielding $[Cr(CNMe)_5(NO)][SFO_3]_2$ (ref. 106). Alkali metal salts of $CpM(CO)_3^-$ react with chlorocarbonylferrocene to produce $CpFe(\eta^5-C_5H_4C(O)W(CO)_3Cp)$ and the decarbonylate $CpFe(\eta^5-C_5H_4-Mo(CO)_3Cp)$ in the case of M=Mo (ref. 107). Irradiation of $[CpMo(CO)_3]_2$ with visible light (5) in halogenated solvents was observed to afford the $CpMo(CO)_3X$ derivatives (ref. 108).

$$[CpMo(CO)_3]_2 \xrightarrow[CHX_3]{h\nu} 2CpMo(CO)_3X \qquad (5)$$

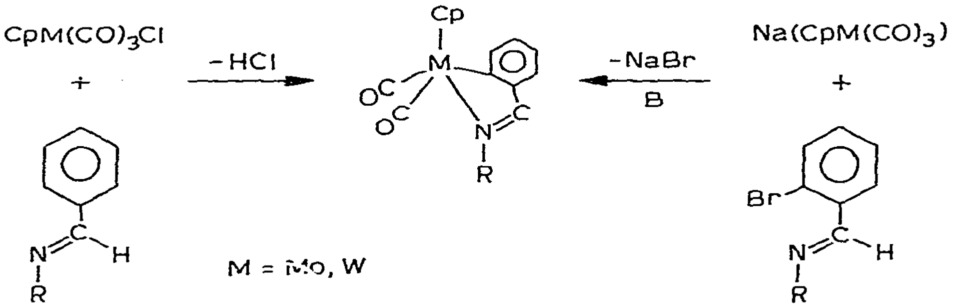
The preparation of $CpW(CO)_2LX$ where L is a phosphine or phosphite and X is Me, $GeMe_3$ or $PbMe_3$ is effected by reaction of $CpW(CO)_2L^-$ with the appropriate iodo-group IVa moiety (ref. 109). Analogous silicon complexes could not be formed. A rather detailed analysis of ^1H, ^{31}P, and ^{13}C NMR data was included (ref. 109). Photolysis of $Me_2Sn[Mo(CO)_3Cp]_2$ as well as $Me_2SnCl[Mo(CO)_3Cp]$ yields $[CpMo(CO)_3]_2$, unlike Me_2Sn and Me_2SnCl derivatives of other metal carbonyls (M=Fe, Co, Mn) which proceed to yield M-M bonds bridged by Me_2Sn and CO (ref. 110). Two of the four isomers which resulted from the reaction of $CpMo(CO)_3Cl$ with (s)-(-)-N-(α-phenylethyl)-1-naphthothioamide were obtained optically pure by fractional recrystallization (ref. 111). Epimerization rates and activation energies were consistent with a configurational change at the molybdenum center (ref. 111). Preparation of cyclopentadienyltricarbonyl (η^1-2-oxopropyl)-molybdenum and -tungsten and (XXXI) are described (ref. 112).



XXXI

Other paramagnetic metallocenes were prepared by reacting 1,3-diphenyl- and 1-methyl-3-phenyl-cyclopentadienyllithium with transition metal salts such as $CrCl_2$ (ref. 113). A detailed analysis of the ^1H NMR and paramagnetic shifts for these complexes was included (ref. 113).

Cyclopentadienyldicarbonyl-molybdenum and -tungsten complexes with chelating ligands derived from Schiff bases of benzaldehyde have been prepared by the reaction sequences given below (ref. 114). Using S-(-)-α-phenylethylamine as the amine component, mixtures of diastereoisomers were formed, from which $(+)_{365}$-Mo and $(+)_{365}$-W complexes could be obtained optically pure by fractional crystallization. Epimerization of these complexes in the temperature range 0°-30°C in toluene was shown to obey a first-order rate law (ref. 114).

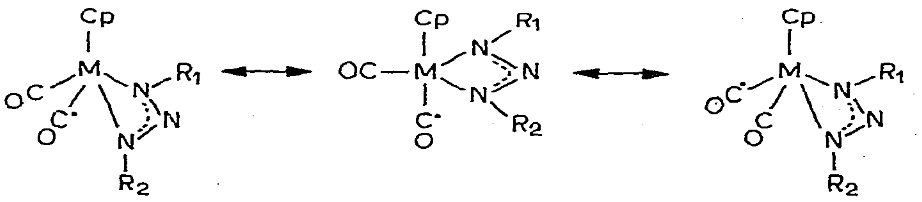


(6)

M = Mo, W

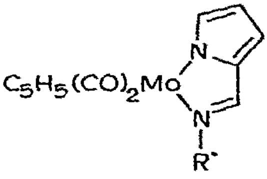
R = $CH(CH_3)_2$, $CH_2C_6H_5$, $CH(CH_3)(C_6H_5)$;

The optical induction of chelate ligands LL' in $CpMo(CO)_2LL'$, where the ligands contain an asymmetric center and two configurations at the molybdenum atom exist, has been investigated by Brunner and coworkers (ref. 115). Typical complexes are illustrated below (XXXII,XXXIII) where $R^*=SCH(CH_3)(C_6H_5)$ (ref. 115).

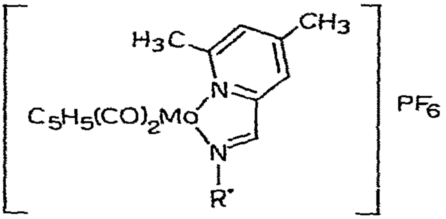


(7)

The Cp(CO)$_2$M(R-$\underline{\text{N-N-N}}$-R') (M=Mo, W; R-aryl and R'=aryl or alkyl) complexes have been prepared from CpMo(CO)$_3$Cl and the corresponding silver triazenide salts (ref. 116). Temperature dependent ^{13}C NMR spectra have shown some of these species to be fluxional involving an interchange of the two CO groups *via* a Berry pseudorotation process (ref. 116). Mass spectral studies of these complexes demonstrate the formation of nitrene type species [(Cp)(CO)$_n$M=NR]$^+$, n=0,

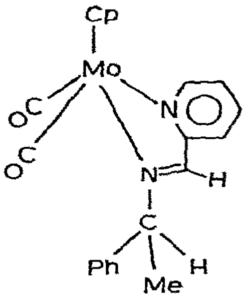


XXXII

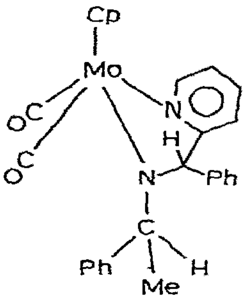


XXXIII

Reaction of PhLi with (XXXIV) in ether at -78° gave 22% (XXXV) (ref. 117).

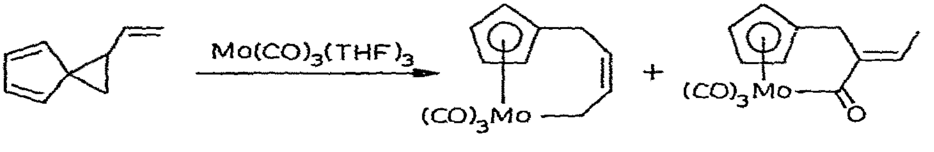


XXXIV



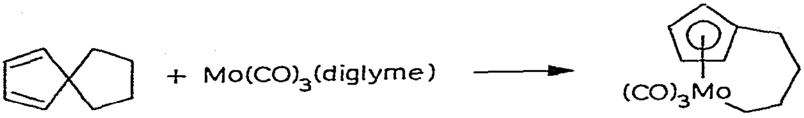
XXXV

Novel alkyl and acyl analogues of CpMo(CO)$_3$C(O)R (XXXVI) (XXXVII) were formed according to the reaction below (ref. 118).

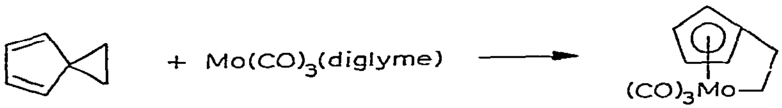


XXXVI XXXVII (8)

The interesting transformation illustrated in (8) suggested a diene-metal carbonyl precursor-intermediate which was in fact observed for the analogous iron derivative in this and a previous work (ref. 119).

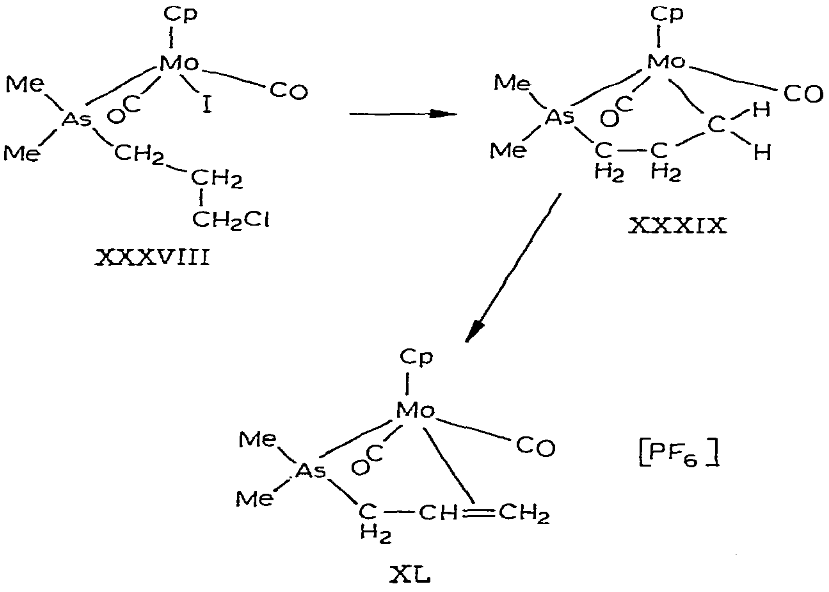


(9)



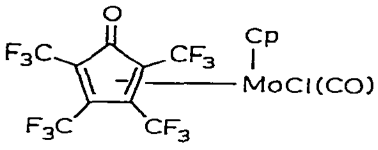
(10)

Sodium amalgam reduction of complexes such as (XXXVIII) produces the arsinometallocycle complex (XXXIX) which reacts with $Ph_3C^+BF_4^-$ yielding (XL) (ref. 120). The stereochemical non-rigidity of (XL) is rationalized according to a sp-tbp isomerization process (ref. 120).



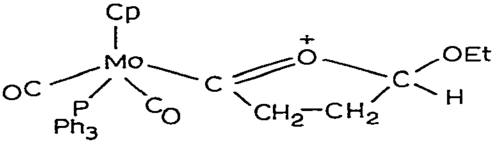
(11)

Reaction of $F_3CC \equiv CCF_3$(1) with $MoCl(CO)_3(Cp)$ gives the cyclopentadienone complex $MoCl(CO)[(CF_3)_4C_5O](Cp)$ (XLI) (ref. 121). If the displaced CO is removed, the product is $MoClL_2(Cp)$ together with minor amounts of [MoCl(L)(Cp)]. Reaction of L with $WCl(CO)_3(Cp)$ gives only $WClL_2(Cp)$ which was structurally identified by x-ray crystallography as an octahedral 16-electron species in which the acetylene acts as a 2 electron donor (ref. 121).



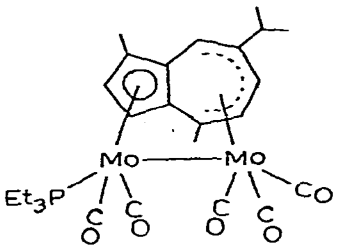
XLI

The extraction of an ethoxide anion from trans-$CpMo(CO)_2(PPh_3)C(O)CH_2CH_2C(OEt)_2H$ by BF_3 in ether has been found to afford the cationic complex (XLII) in 91% yield (ref. 122). The saturated carbon atom in this cyclic ligand is unusually reactive, with a variety of reactions involving this carbon center being described (ref. 122).

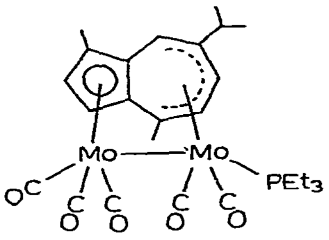


XLII

Larger rings. Studies of cycloheptatrienyl derivatives of Mo included the synthesis of $[Mo(\eta^7-C_7H_7)(\eta^6-C_6H_6)][BF_4]$, $[Mo(acac)(H_2O)(\eta^7-C_7H_7)]^+$, $[MoX(acac)(\eta^7-C_7H_7)]$ and $[Mo_2X_3(\eta^7-C_7H_7)_2]$ (ref. 123). The last compound possesses an unsymmetrical or mixed-valence ground state, as indicated by electronic absorption and ESCA measurements (ref. 124). Chemical synthesis employing metal evaporation techniques have been used to synthesize $Cr(C_7H_7)(C_7H_{10})$, $Cr(C_7H_8)(PF_3)_3$, metal carbonyls (e.g., $Cr(CO)_6$), and anhydrous metal acetylacetonates (ref. 125). Green and Pardy have reported the synthesis of the compounds $[Mo(\eta^7-C_7H_7)(dppe)Y]$ (Y=Cl, I, Me, H), $[Mo(\eta^7-C_7H_7)(dppe)Cl]^+A^-$ ($A^-=PF_6^-$ or I^-), and $[Mo(\eta^7-C_7H_7)(dppe)L]^+PF_6^-$ (L=CO, MeCR or dppe) (ref. 126). Reaction of (guaiazulene)$Mo_2(CO)_6$ with PEt_3 produces the two isomers, (XLIII) and (XLIV) (ref. 127). Temperature dependent ^{13}C NMR studies on these complexes aided in determining that the cyclopentadienyl-bound $M(CO)_3$ fragment of the parent hexacarbonyl is more internally labile. Further studies showed that the presence of alkyl substituents on the azulene ring in the parent hexacarbonyl had only a small effect on the fluxionality (ref. 128). Similarly, the effect of the metal (comparing Mo to W) is inconsequential to rates of CO scrambling (ref. 128).



XLIII



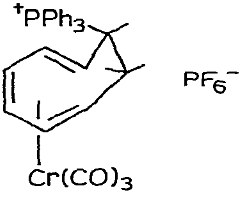
XLIV

The aryl-sulfinato complexes η^7-$C_7H_7Mo(CO)_2SO_2R$ have been synthesized by reaction of η^7-$C_7H_7Mo(CO)_2I$ with the Ag-SO_2-R compounds (ref. 129). The sulfinate group is S-bonded. Mononuclear and dinuclear thioaryl complexes were isolated by reaction of η^7-$C_7H_7Mo(CO)_2Br$ with aryl mercaptans R'-S-H in the presence of $(C_2H_5)_3N$ which functioned as a proton acceptor (ref. 129). IR data indicate the dependence of the π-acceptor abilities of the sulfur atom from R' (ref. 129). Reaction of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]\,[PF_6]$ with ditertiary phosphine ligands afforded products of three types; the monosubstituted complexes $[LM(CO)_2Ph_2P(CH_2)_nPPh_2]$-$[PF_6]$ (L=η^7-C_7H_7, M=Mo, n=1); the chelated complexes $[LM(CO)Ph_2P(CH_2)_nPPh_2]$-$[PF_6]$ (L=η^7-C_7H_7, M=Mo, n=1 and 2); and the dinuclear complex $[(\eta^7\text{-}C_7H_7)Mo\text{-}(CO)_2]_2\text{-}[\mu\text{-}Ph_2PCH_2CH_2PPh_2][(PF_6)_2]$ (ref. 130).

Contrary to previous reports, Kane-Maguire and coworkers have demonstrated that formation of the phosphonium adducts $[(C_7H_7PBu_3)M(CO)_3]^+$ is the first detectable reaction upon treating $[(C_7H_7)M(CO)_3]^+$(M=Cr, Mo, W) cations with tri-n-butylphosphine with subsequent steps leading to $(Bu_3P)_3W(CO)_3$ (12) (ref. 131).

$$[(C_7H_7)M(CO)_3]BF_4 + PBu_3 \xrightarrow{\text{acetone}} [(C_7H_7PBu_3)M(CO)_3]BF_4 \xrightarrow[\text{acetone}]{\text{excess } PBu_3} [(PBu_3)_3M(CO)_3] + [C_7H_7PBu_3]BF_4 \tag{12}$$

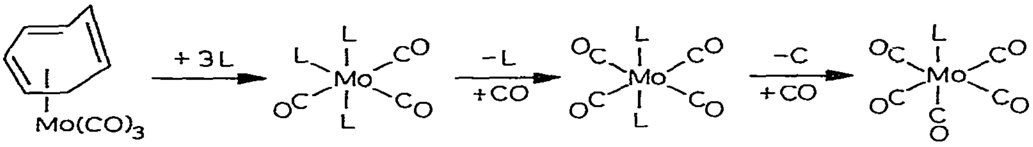
Phosphonium salts such as $[[C_7H_7\cdot P(OBu)_3]Cr(CO)_3]BF_4$ resulted from the addition of $P(OBu)_3$ to $[(C_7H_7)Cr(CO)_3]BF_4$ (ref. 132). A kinetic investigation of the *similar reaction with* $P(n\text{-}Bu)_3$ *established that* $rate=k[complex][P(n\text{-}Bu)_3]$ (ref. 133). Within the VIB metal series k is roughly independent of metal, however, there is a difference between analogous metal complexes with $(C_6H_7)Fe(CO)_3^+ > (C_7H_7)Cr(CO)_3^+ >> (C_6H_6)Mn(CO)_3^+$ (ref. 133). An investigation of the reaction of $[C_8H_9Cr(CO)_3]PF_6$ with PPh_3 at low temperatures produced an orange powder that precipitates on addition of the ether and analyses as $[C_8H_9PPh_3Cr(CO)_3]PF_6$ (XLV).



XLV

The reaction of tropylium and homotropylium complexes of molybdenum and tungsten with alkylphosphines has been investigated by Salzer. Ring addition is observed when low temperatures are maintained, while ring- or CO-substitution occurs at room temperature (ref. 135). A mechanistic scheme for these reactions is proposed. The compound $[C_7H_7Mo(CO)_2L]^+$ is attacked by $P(i\text{-}Pr)_3$ at the carbocyclic ring, giving a phosphonium salt (ref. 135).

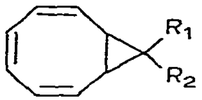
Tricarbonyl-η-1,3,5-cycloheptatriene-chromium(0) reacts photochemically with trimethyl-phosphine, -arsine, or -phosphite respectively to form the complexes $CrC_7H_8(CO)_2L$ ($L=P(CH_3)_3$, $As(CH_3)_3$, $P(OCH_3)_3$ and $CrC_7H_8(CO)[P(OCH_3)_3]_2$. The ^1H, ^{13}C and ^{31}P NMR spectra of these complexes are temperature dependent as a result of a hindered motion of the C_7H_8 ligand (ref. 136). Reactions of cycloheptatrienemolybdenum tricarbonyl, $C_7H_8Mo(CO)_3$, with maleic acid or fumaric acid esters (L) at 60-80°C do not give the expected mononuclear tricarbonyl derivatives, $Mo(CO)_3L_3$ but yield binuclear CO-bridged complexes $[Mo(CO)_3L_2]_2$ in which the ester molecules are π-coordinated across the C:C double bond (ref. 137). The binuclear complexes $[Mo(CO)_3L_2]_2$ (L=maleic acid or fumaric acid esters) react with 2,2'-bipyridine or 1,10-phenanthroline with elimination of CO giving the mononuclear dicarbonyl compounds $Mo(CO)_2QL_2$ (Q=bipy,ophen) with cis-carbonyl ligands (ref. 138). In the reaction of ophen and fumaric acid esters with $C_7H_8Mo(CO)_3$, tricarbonyl complexes mer-$Mo(CO)_3$(ophen) with a meridional arrangement of the CO ligands are formed (ref. 138). A variety of substituted thioureas have been found to react with cycloheptatrienemolybdenum tricarbonyl to yield the $Mo(CO)_5$(thiourea) derivatives (13) (ref. 139). On the other hand, these sulfur donor ligands react with $Mo(CO)_4B$ (B=o-phen or bipy) to afford the mixed ligand derivatives $Mo(CO)_3BL$ (ref. 139). Infrared spectroscopy in the ν(CO) region was used to characterize these derivatives (ref. 139).



(13)

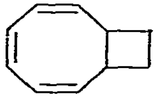
Addition of $(BuO)_3P$ to $[(C_7H_7)Cr(CO)_3]BF_4$ gave a novel phosphonium salt which is remarkably stable (ref. 140).

The preparation of the compounds (triene)$M(CO)_3$ (M=Mo, W) are described where the triene ligands are bicyclic derivatives of cyclooctatriene as shown below (XLVI,XLVII) (ref. 141). These tricarbonyl complexes of molybdenum were found to readily react with carbon monoxide to afford the corresponding (triene)Mo-$(CO)_4$ derivatives. Although it was generally found that these ligands are stabilized against valence isomerization by complex formation, bicyclo-[6.2.0]-deca-2,4,6-triene $Mo(CO)_3$ rearranges at 125° to give bicyclo[4.2.2]deca-2,4,7-triene $Mo(CO)_3$ (XLIX) (ref. 141).

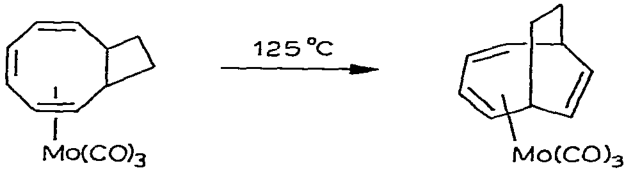


XLVI

$R_1 = H,\ R_2 = H$
$R_1 = H,\ R_2 = CH_3$
$R_1 = Cl,\ R_2 = H$
$R_1 = CO_2C_2H_5,\ R_2 = H$



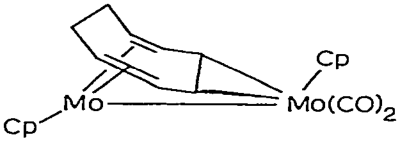
XLVII



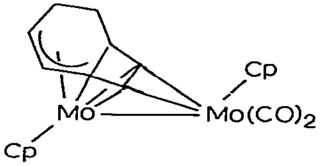
XLVIII XLIX

(14)

The reaction of cyclooctatetraene with $[CpMo(CO)_3]_2$ in refluxing octane proceeds with CO loss and 1,4 hydrogen migrations within the ring to yield (L) (ref. 142). In polar solvents further rearrangement occurs, yielding (LI). X-ray crystal studies confirmed the structures of the two isomers (ref. 142).

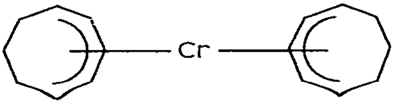


L

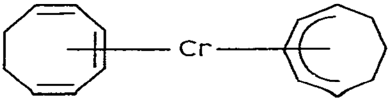


LI

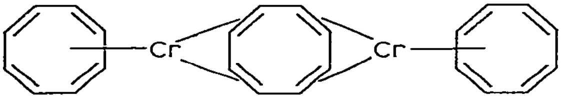
The _in situ_ reduction of $CrCl_3$ by ($\underline{i}$-C_3H_7)MgBr in the presence of the appropriate 8-membered cyclic diene, triene, or mixtures yielded the π-complexes (LII), (LIII), and (LV). Dehydrogenation of (LII) yielded (LIV) (ref. 143).



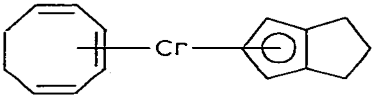
LII



LIII



LIV

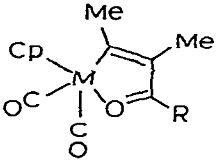


LV

Alkyls and Hydrides

Alkyls. In the presence of B_2H_6/C_6H_6 the molybdenum acetyl complex $[(Cp)(CO)_2(PPh_3)Mo(COCH_3)]$ has been observed to undergo smooth reduction to the $[(Cp)(CO)_2(PPh_3)MoCH_2CH_3]$ derivative with concurrent $[(Cp)(CO)_2(PPh_3)MoH]$ formation (ref. 144). Several σ-alkyl-π-cyclopentadienyltungsten tricarbonyl derivatives, $CpW(CO)_3R$ (R=i-Pr, n-Bu, sec-Bu, n-Am and i-Am) have been prepared and their infrared spectra in the ν(CO) region discussed (ref. 145). The bridged carbyne complex, $(Me_3SiCH_2)_2W(\mu\text{-}C\text{-}SiMe_3)_2W(CH_2SiMe_3)$ was prepared by the reaction of $(Me_3SiCH_2)_2Mg$ and WCl_4 in THF (ref. 146). In hydrocarbon solvents only $W_2(CH_2SiMe_3)_6$ was obtained (ref. 146).

The perfluoromethyl derivative, $CpMo(CF_3)(CO)_3$ reacts with but-2-yne photochemically to form the 16-electron species $CpMo(CF_3)(CO)(MeC_2Me)$ (ref. 147), however the more electron-rich methyl and benzyl derivatives of Mo and W react to give the oxymetallocycle, or vinylketone derivative (LVI) (ref. 148). Further reactions of (LVI) with $MeC\equiv CMe$ and other ligands such as isocyanides, phosphines and CO are also reported.

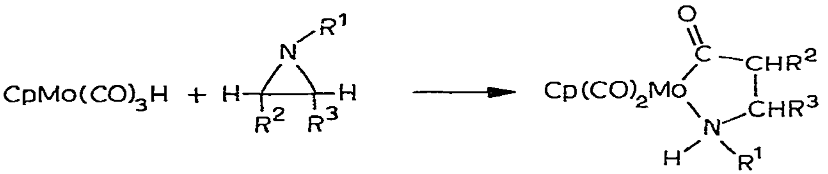


M = Mo, W; R = Me, CH_2Ph, CF_3

LVI

$CpMo(CO)_2(CH_3C{:}NC_6H_5)$ was prepared by treating $[(Cp)Mo(CO)_2C\equiv NC_5H_5]^-$ with MeI in THF (ref. 149). An x-ray crystal structure analysis shows the presence of a π-bonded iminoacyl group (ref. 149). The product is formed by isocyanide insertion into a Mo-Me bond with incorporation of the N atom into the coordination sphere of the Mo atom (ref. 149). Reaction of $M(Cp)(CH_2R)(CO)_3$ (M=Mo, W; R=3-, 4-pyridylium;) with $Tl(ClO_4)_3$ in aqueous acidic solution involved a rapid two-electron oxidation followed by a series of reactions giving the corresponding pyridinioacetic acid as the main organic product (ref. 150). The reaction between 1- and 2-trialkylsilyl-3-chloroprop-1-ene and various metal complexes gave η^1- and η^3-silylallyl complexes of Mo and W (ref. 151). The general reactions employed involve the use of metal anions in a salt elimination reaction and oxidative addition reactions (ref. 151). Carbon dioxide was found to attack the W-N bond of $W_2Me_2(NEt_2)_4$ to yield oxygen-bound CO_2 insertion products, retaining the $W\equiv W$ bond and the W-C bond (ref. 152). X-ray crystal structure analysis showed the carbamato ligands act as monodentate, non-bridging bidentate and bridging bidentate ligands; in solution these are readily equilibrated as evidenced by NMR studies (ref. 152). A new σ-bonded alkyl derivative of tungsten (VI), $MeWCl_5$ was prepared from WCl_6 and $HgMe_2$ (ref. 153). The reaction of this species with simple unidentate ligands gave extensive reduction, and adducts were obtained with bidentate ligands, e.g., $MeWCl_5$(diphos) (ref. 153). Spectroscopic (UV/Vis) detection of $[RCr(H_2O)_5]^{2+}$ (R=alkyl, phenyl) as intermediates in the reduction of organic peroxides by Cr^{++} was used to suggest the nature of various alkoxy-radicals produced during the reduction process (ref. 154). An expanded group of $(H_2O)_5CrR^{++}$ complexes were investigated as to the kinetics of R^- transfer to Hg^{++} or $MeHg^+$, forming RHg^+ or MeHgR, respectively, and $Cr(H_2O)_6^{3+}$ (ref. 155). The reaction rate expression was first order in each reagent and the rates depend on R. Electron withdrawing groups (e.g., EF_3) and substituents retarded the rates of reaction. Enormous (<-100 e.u.) negative entropies of activation were reported (ref. 155). Several members of the family of $(H_2O)_5CrR^{2+}$ complexes react cleanly with the interhalogen molecule, IBr (ref. 156). Products of reaction are exclusively the organic iodide RI, $Cr(H_2O)_6^{3+}$, and Br^-; RBr and $(H_2O)_5CrBr^{2+}$ are not formed (ref. 156).

Hydrides. When sodium borohydride was allowed to react with $CpCrCl_2 \cdot THF$, hydrido species such as $CpCrH_2 \cdot THF$ and $CpCr(BH_4)_2$ resulted but were not isolated (ref. 157). In the presence of $P(OMe)_3$ however, the complex $CpCr[P(OMe)_3]_3H$ was obtained; the chemical and dynamical structural properties of the compounds were studied (ref. 157). Studies of the dependence of equivalent conductance on concentration for several transition metal-organic salts suggested that most exist as ion-pairs in the common solvent, THF. Included in this study were $Et_4N^+\mu\text{-}H[Cr(CO)_5]_2^-$ and $Li^+Mo(CO)_5C(O)Ph^-$ (ref. 158). The bridging hydride complex $\mu\text{-}H[W(CO)_5][W(CO)_3(NO)P(OMe)_3]$ may be readily prepared by stirring $\mu\text{-}H[W_2(CO)_9NO]$ with $P(OMe)_3$ in hexane at room temperature (ref. 159). X-ray crystal structure analysis shows the $P(OMe)_3$ to be on the W bearing the NO (which is itself trans to the -H-) and cis to the -H-W-NO linkage. A review of W-H-W complexes is included (ref. 159). Optically active aziridines react with $CpMo(CO)_3H$ stereospecifically maintaining chirality at the two carbon centers and creating two new chiral centers at Mo and N, (LVII) (ref. 160). The resulting complex (LVII) did not epimerize in solution (ref. 160).

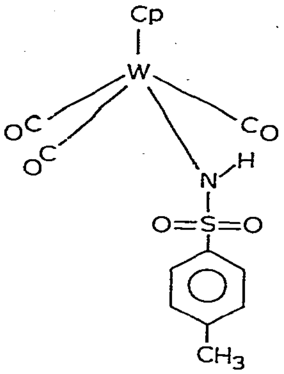


(15)

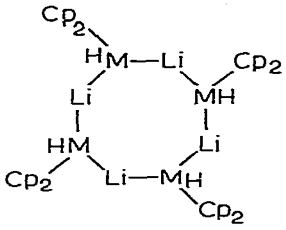
LVII

At low temperatures $CpW(CO)_3H$ reacted with p-toluenesulfonylazide with loss of N_2 to produce the amido derivative (LVIII) (ref. 161).

$MH_2(Cp)_2$ (M=Mo, W) with RLi (R=Me, Ph, Bu) gave the tetramers (LIX) (M=Mo, W) (ref. 162). (LIX) reacted with various organic compounds, e.g. with $PhCH_2Br$ and PhCOCl to give $M(CH_2Ph)_2(Cp)_2$ and $MH(Cp)_2(COPh)$, respectively. With CO_2 (LIX) gave $M(Cp)_2(CO)$ and with CO, the Mo tetramer gave both $Mo(Cp)_2(CO)$ and the cyclopentenyl compound $Mo(Cp)(n^3\text{-}C_5H_7)(CO)_2$ (ref. 162).



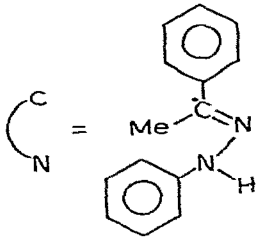
LVIII

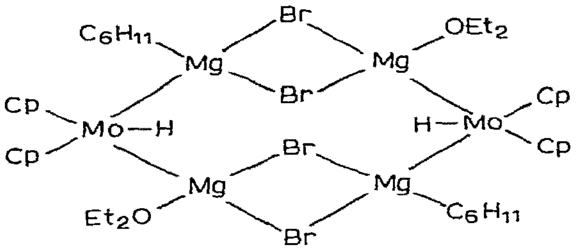


LIX

Metal-Metal Bonded Complexes

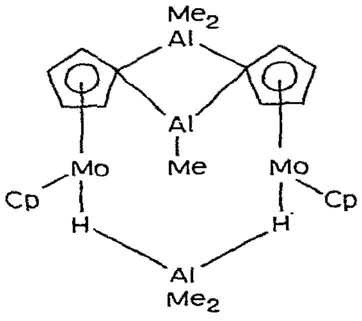
$(Cp)_2W_2(CO)_6$ has been shown to react with the amines (L) (L=ethyl-, isopropyl-, diethyl-, butyl-, and cyclohexyl-amine) at room temperature to give $(Cp)_2W_2(CO)_5L$ derivatives (ref. 163). Similar complexes were formed by the potentially chelating ligands ethylenediamine, o-phenanthroline, and 2,2'-bipyridine (ref. 163). Reduction of these amine derivatives with sodium amalgam with subsequent treatment with $Mn(CO)_5Br$ afforded the mixed metal species, $[(Cp)W(CO)_2L]Mn(CO)_5$ and $[(Cp)W(CO)_3]Mn(CO)_5$, which were separated by column chromatography (ref. 163). $Cp_2M_2(CO)_6$ (M=Mo and W) underwent efficient photoheterolysis to a metal carbonyl anion on irradiation in solvents of high donicity (ref. 164). Retention of configuration in the replacement of Cl^- by $CH_2SiMe_3^-$ was observed in the reaction of anti-$W_2Cl_2(NEt_2)_4$ and $LiCH_2SiMe_3$ (ref. 165). Isomerization of the kinetically controlled product to the thermodynamically favored gauche-$W_2(CH_2SiMe_3)_2(NEt_2)_4$ was monitored by NMR and activation energy parameters computed (ref. 165). $(Cp)_2Mo_2(CO)_4(\mu\text{-EtC}\equiv\text{CEt})$ has a molecular structure that lacks symmetry (ref. 166). Two (Cp)Mo groups are connected by a Mo-Mo bond of 2.977(1) Å with the usual sort of crosswise acetylene bridge. There are two terminal CO groups on Mo(1) and one on Mo(2). The 4th CO group is in a semi-bridging posture with Mo(2)-C = 1.936(6) and Mo(2)-C = 2.826(6) (ref. 166). The reaction of Pd(C-N)LCl (L=pyridine, C-N=(LX)) with $Mo(CO)_3(Cp)$ has afforded a bimetallic Pd-Mo complex (ref. 167). On the other hand, due to steric hindrance, the analogous process with the palladium complexes where $L=PEt_3$ and PPh_3 was found not to occur (ref. 167). Reaction of this bimetallic complex with PPh_3 led to metal-metal bond cleavage with formation of $[Pd(C\text{-}N)PPh_3Py][Mo(CO)_3(Cp)]$. This ionic complex decomposes with loss of pyridine and C-N ligands to give the new tetrametallic $[PPh_3PdMo(CO)_3(Cp)]_2$ cluster (ref. 167).



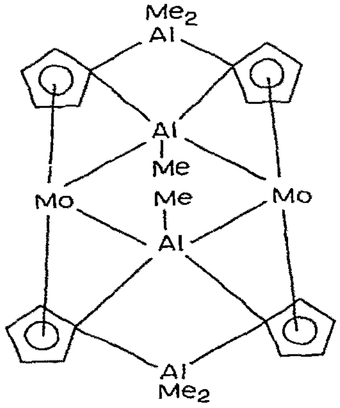


LXI

$Mo(Cp)_2H_2$ with $Mg(C_6H_{11})Br$ (C_6H_{11}-cyclohexyl) gave the cyclic dimer (LXI), and with MgRX (e.g. RX=BuBr, PhBr) gave similar adducts $Mo(Cp)_2H_2 \cdot MgRX$ (ref. 168). $Mo(Cp)_2H_2$ with $AlMe_3$ gave the complexes LXII and LXIII which contained Mo-Al bonds (ref. 169).



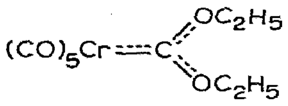
LXII



LXIII

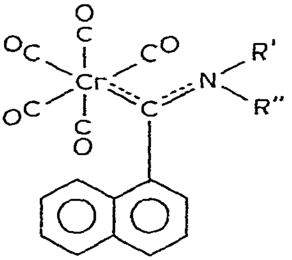
Carbenes and Carbynes

Carbenes. Biscarbene complexes, cis-$M(CO)_4L_2$ (M=Cr, Mo, W), with cyclic carbene ligands (L=1,2-dimethyl-4-pyrazolin-3-ylidene, 1,3-dimethyl-4-imidazolin-2-ylidene, 2,4-dimethyl-1,2,4-triazolin-3-ylidene and 1,3-dimethyl-benzimidazolin-2-ylidene) were prepared by thermal disproportionation of $M(CO)_5L$ at 100-150°C, and the photo-induced conversion to the corresponding trans-isomers was investigated (ref. 170). Fischer and co-workers have prepared the diethoxycarbene derivative of chromium pentacarbonyl from the reaction of $Cr(CO)_6$ with KOC_2H_5 followed by alkylation with $[(C_2H_5)_3O]BF_4$ (ref. 171).



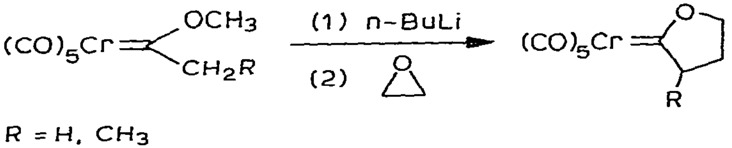
$$(CO)_5Cr{=}C(OC_2H_5)_2$$

Brunner, Doppelberger, Fischer and Lappus have synthesized a series of chiral aminocarbene pentacarbonylchromium(0) complexes containing a 1-napthyl or 2-naphthyl group at C(carbene (LXIV)) (ref. 172). It was demonstrated by ^1H NMR spectroscopy that rotation around the aryl-C (carbene) bond was highly restricted in the 1-naphthyl derivatives at temperatures up to +80°C, whereas in the 2-naphthyl derivatives rotation was rapid down to -90°C (ref. 172).



LXIV

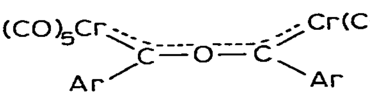
(2-Oxacyclopentylidene)pentacarbonylchromium(0) and (5-methyl-2-oxacyclopentylidene)pentacarbonylchromium(0) have been prepared from the reaction of the corresponding carbene complexes and ethylene oxide (LXV) (ref. 173). The thermodynamic acidities of these two derivatives were found to be nearly equal. The rate of the base catalyzed deuterium exchange for R=H is 1.57 times faster than that for $R=CH_3$, whereas the reactivity of the anions generated from the hydrogen complex is 2.6-5.2 times less than that of anions generated from the methyl complex (ref. 173).



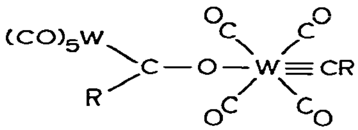
LXV

Hydroxycarbene complexes may be dehydrated to yield binuclear carbene anhydrides of the form (LXVI) (ref. 174). Chemical characterizations of (LXVI) included reaction with dimethylamine which yielded the aminocarbene, $(CO)_5CrC(Ar)NMe_2$ and the dimethylammonium salt of pentacarbonylchromiumbenzoate. Tetraalkylammonium halides reacted with (LXVI) to yield the carbyne complex, trans-$(X)Cr(CO)_4(\equiv CAr)$ as well as $[NR_4][(CO)_5CrC(O)Ar]$ (ref. 174).

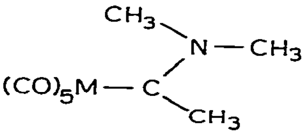
With tungsten as central metal, however, the dehydration of $(CO)_5WC(OH)Ar$ or $(CO)_5WC(OH)Me$ yielded the binuclear carbyne complexes (LXVII) (ref. 175).



LXVI



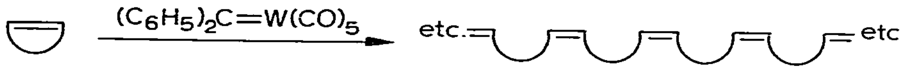
LXVII



LXVIII

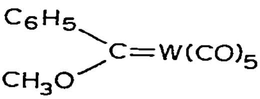
Fischer and co-workers have described the preparation and spectral properties (mass spectrum, ^1H and ^{13}C NMR, and $\nu(CO)$) of chlorodiethylaminocarbene-pentacarbonyl chromium from ethoxydiethylaminocarbene-pentacarbonyl chromium and BCl_3 (ref. 176). Attempts to prepare the analogous fluorocarbene derivative via reaction of $Cr(CO)_5C(NEt_2)(OEt)$ with BF_3 led to the carbyne complex $[Cr(CO)_5(\equiv CNEt_2)][BF_4]$, which was isolated and characterized (ref. 177). Treatment of this carbyne complex with $[n\text{-}Bu_4N]F$, however led to the desired $Cr(CO)_5C(F)(NEt_2)$ (ref. 177). ^{13}C-^{15}N coupling constants in methyldimethylaminocarbene-pentacarbonyl derivatives of chromium and tungsten have been reported (ref. 178). These parameters were used to provide bonding information in these species.

Katz, Lee and Acton found that (diphenylcarbene)pentacarbonyltungsten, without added cocatalysts, is an effective initiator of metatheses of numerous cis-cycloalkenes, converting them into polyalkenamers 90% or more of whose double bonds are cis (LXIX) (ref. 179).



LXIX

They also examined whether molecule (LXX) would react with cyclobutene and norbornene (ref. 180). The fact is that (phenylmethoxycarbene)pentacarbonyltungsten in small amounts brings about metatheses of both to the corresponding polyalkenamers, and the stereochemistries of the transformations are remarkable (ref. 180).



LXX

In marked contrast to the reaction of $M(CO)_5C(R')R''$ with PR_3 at low temperatures which yielded phosphine-carbene carbon adducts, no such complexes were observed in similar reactions with heavier VA donor ligands (ref. 181). At higher temperatures carbonyl as well as carbene substitution products, such as cis/-trans-$(CO)_4Cr(L)C(OMe)Me$, $LCr(CO)_5$ and trans-$L_2Cr(CO)_4$ ($L=AsR_3$, SbR_3 and PR_3), were observed (ref. 181). Fischer and Held have reported the synthesis of pentacarbonyl π-olefin complexes of tungsten from the reaction of $(CO)_5WC(OMe)Ph$ with alkyllithium reagents (17) (ref. 182).

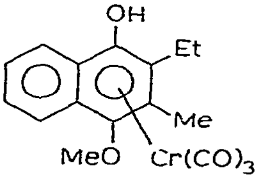
$$(CO)_5WC(OCH_3)Ph \xrightarrow[(2)SiO_2/Pentane/-40°C]{(1)RCH_2Li/Ether/-78°C} (CO)_5W{=}C(CH_2R)Ph + (CO)_5W(HCR{=}CHPh) \qquad (18)$$

Boron trifluoride promotes ethanol loss in pentacarbonyl-(3-dimethylamino-3-phenyl-1-ethoxy-2-propenyldiene)chromium and -tungsten (LXXI) yielding the allenylidene complex (LXXII) (ref. 183).

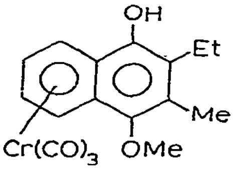
$$(CO)_5MC(OEt)CH{=}C(NMe_2)Ph \xrightarrow[THF]{BF_3} (CO)_5M{=}C{=}C{=}C(NMe_2)Ph \qquad (19)$$

At room temperature the homolysis product of the $PhLi/Cr(CO)_5C(OMe)Ph$ adduct, $Li^+[(CO)_5CrC(OMe)Ph_2]^-$, is $Ph_2(MeO)C-C(OMe)Ph_2$ (ref. 184). A similar product was obtained on reacting the alkoxycarbene with ICN, i.e., $Ph(MeO)(CN)C-C(CN)-(OMe)Ph$ (ref. 184). In another reaction of alkoxycarbene complexes, 2-pentyne reacted with $Cr(CO)_5C(OMe)Ph$ at 45°C to yield (LXXIV) and at 90°C to yield (LXXV) (ref. 185).

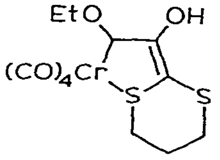
A carbene-thio-carbonyl complex (LXXVI), characterized by a crystal structure determination, was prepared by the reaction of $Li[CHS(CH_2)_3S]$ with $Cr(CO)_6$, followed by ethylation with $[Et_3O][BF_4]$ (ref. 186). The proposed mechanistic scheme involved a hydroxycarbene intermediate (ref. 186).



LXXIII

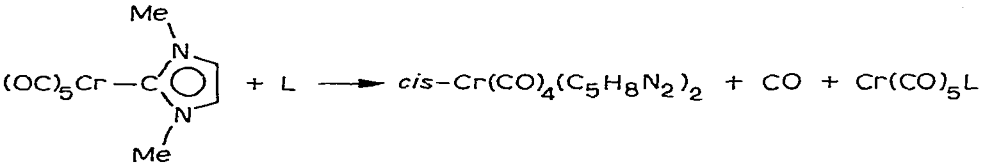


LXXIV

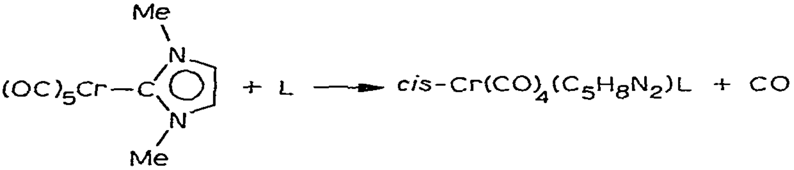


LXXV

Thermal disproportionation of the 1,3-dimethyl-4-imidazolin-2-ylidene metal pentacarbonyl (metal=Cr, Mo, W) yielded $M(CO)_6$ and cis-$(CO)_4M(C_5H_8N_2)_2$ (ref. 187). Ligand substitution reactions proceed as illustrated in (20 and 21) where $L=P(\underline{c}-C_6H_{11})_3$ or py, and $L'=PPh_3$ or $CN(\underline{c}-C_6H_{11})$. Hindered rotation about the cyclic carbene ligand was studied by ^{1}H NMR (ref. 187).



(20)



(21)

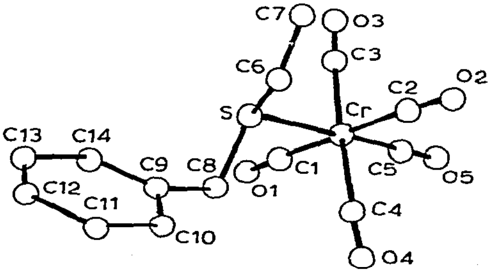
The reaction (22) of $(CO)_5CrC(R)NH_2$ ($R=CH_3$, C_6H_5) with aminoacetylene has been described by Dotz (ref. 188).

$$(CO)_5CrC(R)NH_2 + CH_3C{\equiv}CN(Et)_2 \xrightarrow[20^\circ]{C_6H_6} (CO)_5CrC(R)(N{=}C(Et)NEt_2) \qquad (22)$$

Further rearrangements of the acetylene insertion product from reaction (23) led to metallocyclic derivatives (ref. 189).

$$(CO)_5CrC(OMe)Ph + Et_2NC{\equiv}CNEt_2 \rightarrow (CO)_5Cr{-}C(NEt_2)(C(NEt_2){=}C(OEt)Ph) \qquad (23)$$

The carbene complexes $[(CO)_5CrC(OC_2H_5)R]$ (R=Bu, Ph) have been found to react with the sulfides SR^1R^2 ($R^1=C_2H_5$; $R^2=C_2H_5$, CH_2Ph) to afford the neutral pentacarbonyl(thio)chromium(0) complexes $[(CO)_5CrSR^1R^2]$ (ref. 190). The complexes were fully characterized by chemical analysis, IR, NMR, and mass spectroscopy. In addition the structure of one of these, $(CO)_5CrS(C_2H_5)CH_2Ph$, was confirmed by a single-crystal X-ray study (LXXVI) (ref. 190).

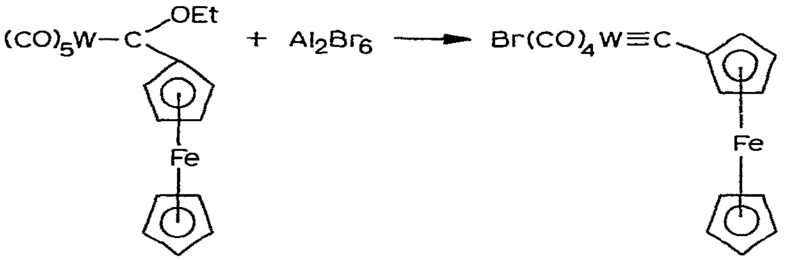


The successful use of carbene complexes as amino protecting groups in peptide synthesis, via the aminolysis of alkoxycarbenes to yield $(CO)_5MC(NHR)R'$, was reported by Fischer and Weiss (ref. 191). The germanium analogue of the carbene ligand, germylene, was synthesized by reaction of (CO)$_5$Cr(GeCl$_2$)·THF with RSSiMe$_3$, thus yielding (CO)$_5$Cr $\leftarrow$ Ge(SR)$_2$ (ref. 192). These complexes could be reacted with BCl$_3$ in petroleum ether to yield the THF-free (CO)$_5$Cr $\leftarrow$ GeCl$_2$ complex (ref. 192). Base stabilized germylenes served as ligands to a broad range of organo-VI-metallics (ref. 193). The photochemically produced complexes included (CO)$_5$MGeCl$_2$·THF, (arene)Cr(CO)$_2{}^-$ GeCl$_2$·NSC$_7$H$_5$, and others (ref. 193). Oxycarbenes of molybdenum were generated by GeCl$_3{}^-$ promoted carbonyl insertion in CpMo(CO)$_3$R yielding CpMo(CO)$_2$(GeCl$_3$)C(O)R$^-$, which were alkylated with R'$_3$O$^+$ reagents (ref. 194). Internal alkylation, yielding cyclic oxycarbenes, was observed when R was -CH$_2$CH$_2$CH$_2$Br (ref. 194).

Carbynes. Several carbyne complexes of the type trans-(X)M(CO)$_4$($\equiv$CR)(X=Cl, Br, I; M=Cr, W; and R=Me, Et, Ph) were prepared by the reaction of BX$_3$ on the alkoxycarbene M(CO)$_5$C(OR')R in pentane in -20°C (ref. 195). All complexes prepared melt with decomposition at temperatures between 0-35°C and hence must be handled cold (ref. 195). Carbon monoxide loss is observed also when cis-LCr(CO)$_4$C(OMe)Me (L-PMe$_3$, AsMe$_3$, or SbMe$_3$) reacts with BX$_3$ (X=Cl, Br, I) thus yielding a meridional isomer of (L)(X)Cr(CO)$_3$($\equiv$CMe) in which the halogen is trans to the carbyne ligand (ref. 196). Several reactions of the chlorocarbene complex Cr(CO)$_5$C(Cl)NMe$_2$ was described in which abstraction of Cl$^-$ yielded the cationic carbyne, Cr(CO)$_5$($\equiv$CNMe$_2$)$^+$ (ref. 197). Reconversion into a carbene complex, Cr(CO)$_5$C(NMe$_2$)$_2$ was effected by addition of LiNMe$_2$ to the carbyne carbon (ref. 197). Fischer and coworkers have synthesized a large number of π-cyclopentadienyl(dicarbonyl)carbyne complexes of tungsten by the procedure described below (ref. 198).

$$\mathrm{Br(CO)_4W{\equiv}C{-}R + LiC_5H_5 \xrightarrow[-50^\circ C]{THF} \pi{-}C_5H_5(CO)_2W{\equiv}C{-}R + LiBr + 2CO} \tag{24}$$

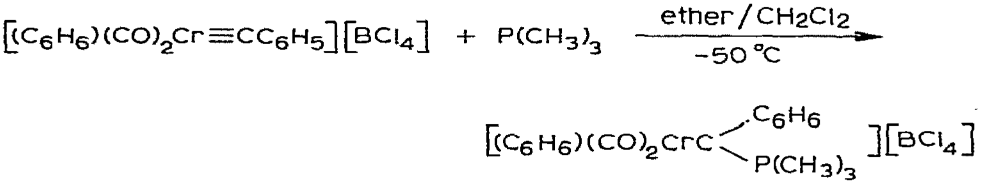
Whereas cis-LM(CO)$_4$C(OMe)R complexes (L=VA donor ligands) react with BX$_3$ to yield L(CO)$_3$(X)M($\equiv$CR), cationic carbyne complexes, [trans-Cr(CO)$_4$ (L)($\equiv$CMe)]$^+$-BX$_4{}^-$, are obtained upon reaction of the trans substituted alkoxycarbene complexes with BX$_3$ (ref. 199). Neither is halide substitution observed in the reaction of (η^6-arene)Cr(CO)$_2$C(OMe)Ph with BCl$_3$, but again a cationic carbyne complex, (η^6-arene)Cr(CO)$_2$($\equiv$CPh)$^+$ is produced (ref. 200). Aminolysis leads to (η^6-arene)Cr(CO)$_2{}^-$C(NR$_2$)Ph (ref. 200). A carbyne derivative (LXXVII), quite air stable in the solid state and containing ferrocene as a substituent on the carbyne carbon, was prepared according to (ref. 201).



(25)

LXXVII

Halo-carbyne complexes such as $BrM(CO)_4(\equiv CPh)$ (M=Cr, Mo, W) could readily be converted to binuclear complexes such as $(CO)_5Re\text{-}Mo(CO)_4(\equiv CPh)$ when reacted with the alkali metal salt of an appropriate transition metal carbonylate (ref. 202). Reaction of cis-$Cr(CO)_4(PMe_3)[:C(OMe)Me]$ with BF_3 gave 65% mer-$(F_3B)Cr(CO)_3$-$(PMe_3)(\vdots CMe)$, which on treatment with water gave 35% [mer-$(H_2O)Cr(CO)_3(PMe_3)$-$(\vdots CMe)]^+BF_4$ (ref. 203). The addition of trimethylphosphine to the carbyne carbon atom of dicarbonylbenzenephenylcarbynechromium tetrachloroborate has been demonstrated by Kreissl and Stückler to afford a cationic metal-substituted yield (LXXVIII) (ref. 204).



$$[(C_6H_6)(CO)_2Cr{\equiv}CC_6H_5][BCl_4] + P(CH_3)_3 \xrightarrow[-50\,^\circ C]{ether/CH_2Cl_2} [(C_6H_6)(CO)_2CrC\begin{smallmatrix}C_6H_6\\ P(CH_3)_3\end{smallmatrix}][BCl_4]$$

(26)

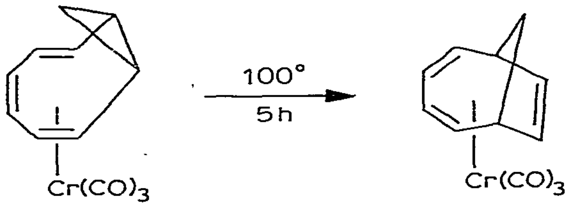
LXXVIII

In contrast, the carbyne complex, $CpW(CO)_2(\equiv C\text{-}C_6H_4Me)$ was found to react with PMe_3 to yield a transition metal substituted ketene, $CpW(CO)(PMe_3)_2C(=C=O)C_6H_4Me$ (ref. 205). The reaction of $Br(OC)_4W{\equiv}CC_6H_4Me\text{-}p$ with PMe_3 gave 86% $Br(OC)_3$-$(Me_3P)WC(:PMe_3)\text{-}C_6H_4Me\text{-}p$ (ref. 206). Fischer and Wagner have shown that trans-$Br(CO)_4W{\equiv}CCH_3$ in the presence of Lewis acids (e.g., $TiCl_4$) is a catalyst for the polymetathesis of cycloolefins (ref. 207).

Olefins, Allyls and Chelates

Olefins. The photochemical synthesis of butadienetetracarbonylchromium and trans,trans-2,4-hexadienetetracarbonylchromium has been described by Koerner von Gustorf and coworkers (ref. 208). The latter complex was shown to be an intermediate in the photocatalytic hydrogenation of trans,trans-2,4-hexadiene with

$Cr(CO)_6$ to give cis-3-hexene (ref. 208). Trans-(NBD)$Cr(CO)_3[P(C_6H_5)_3]$ (NBD= norbornadiene) has been prepared from the low temperature photolysis (NBD)$Cr(CO)_4$ in the presence of $P(C_6H_5)_3$ (ref. 209). The quantum yields of the room temperature photoinduced conversion of (NBD)$Cr(CO)_4$ in the presence of H_2, of $P(C_6H_5)_3$ and of both reagents, were observed to be 0.140, 0.105 and 0.104, respectively (ref. 209). Primary photoinduced formation of monodentate (NBD)$Cr(CO)_4$ was proposed to account for these observations (ref. 209). The triene complex, (bicyclo[6.1.0]nona-2,4,6-triene)molybdenum tricarbonyl, has been observed to react with ^{13}CO in solution to afford stereospecifically the axially labelled ^{13}CO tetracarbonyl derivative (ref. 210). Further reactions of this ^{13}CO derivative with triphenylphosphine or bis (1,2-diphenylphosphino)ethane resulted in formation of the cis disubstituted phosphine derivatives with retention of the ^{13}CO label (ref. 210). The synthesis of the (triene)$Cr(CO)_3$ complexes of bicyclic derivatives of cycloocta-1,3,5-triene has been described by Salzer where triene-bicyclo[1.1.0]nona-2,4,6-triene, 9-anti carbethoxy bicyclo[6.1.0]nona-2,4,6-triene, and bicyclo[6.2.0]deca-2,4,6-triene (ref. 211). The complex where triene-bicyclo[6.1.0]nona-2,4,6-triene was found to rearrange at 100°C to afford bicyclo[4.2.1]nona-2,4,7-triene $Cr(CO)_3$ (LXXIX) (ref 211). Complexes of the general formula (triene)$M(CO)_3P(OPh)_3$ where the triene is bonding to the metal as a diene (M=Mo, W) have been prepared for the first time (ref. 211).



(27)

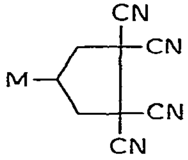
LXXIX

Compounds containing no CO's such as $[Mo(C_3H_5)(arene)(olefin)]^+$ were obtained from the hydrolyzed mixtures of $[AlEtCl_2]_2$, $[Mo(C_3H_5)(arene)\ Cl]_2$ and olefin (olefin=norbornadiene, cyclooctatetraene, or cycloheptatriene) (ref. 212).

Allyls. An extensive series of η^3-allylcarbonyl complexes of molybdenum and tungsten containing 1,2-ethanediylidenediimines (LXXX) as ligands have been prepared by Hsieh and West (ref. 213). The reactions of these complexes with a number of reagents including MeLi, C_5H_5, $SnCl_2$, Ag^+ and Lewis bases have been investigated (ref. 213).

LXXX

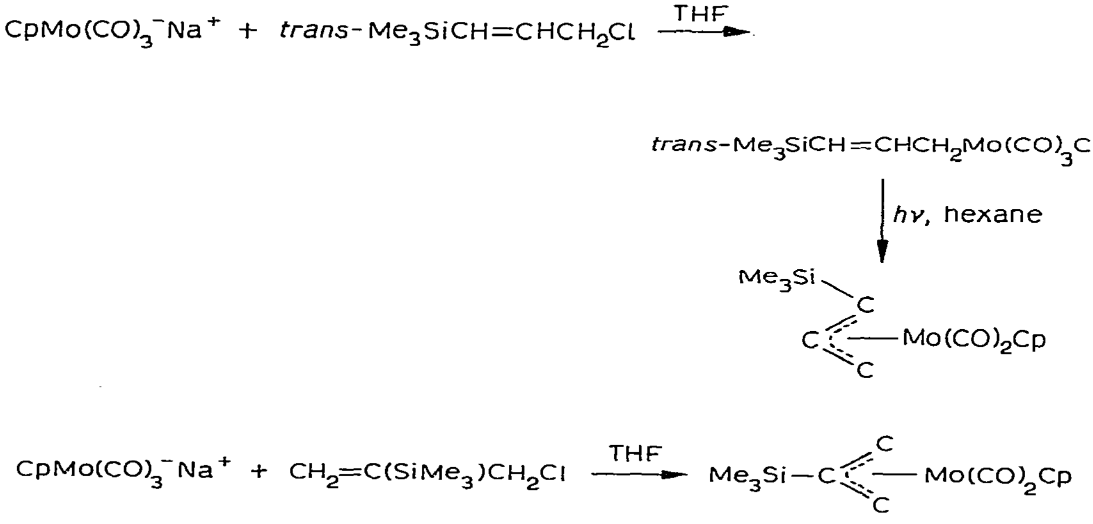
Included in an extensive work regarding the chemistry of η^1-allylic and π-olefinic derivatives of $CpFe(CO)_2$ was a brief account of the reactivities of η-allylic complexes of $CpW(CO)_3$, $CpMo(CO)_3$ and $CpCr(NO)_2$ with tetracyanoethylene to yield the (3+2) cycloaddition products, (LXXXI) (ref. 214).



LXXXI

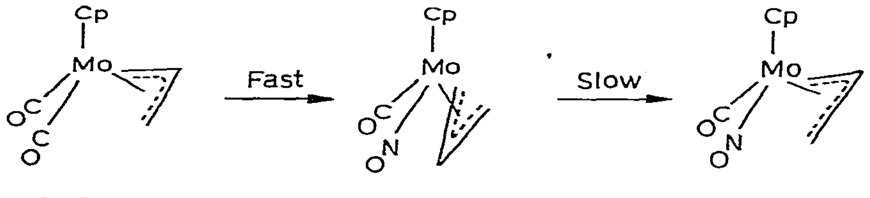
M = $CpMo(CO)_3$, $CpW(CO)_3$ and $CpCr(NO)_2$

η^1- and η^3-silylallyl complexes of molybdenum have been prepared by the reaction sequences shown below (LXXXVII) (ref. 215).



(28)

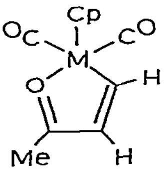
The kinetic product of the reaction of $NOPF_6$ with the endo-exo isomeric mixture of $CpMo(CO)_2(\eta^3-C_3H_5)$, (LXXXII) slowly converts to the thermodynamically more stable exo-π-allylic salt (LXXXIII) (ref. 216). Based on concurrent studies with 2-methylallyl derivatives, it was proposed that a concerted S_E2 attack of NO^+ displaces CO and promotes formation of a η^1-allyl intermediate (ref. 216).



LXXXII

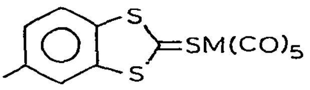
LXXXIII

Chelates. Irradiation of $CpM(CO)_3Me$ (M=Mo, W) in the presence of acetylene gives rise to the metallocyclic complex (LXXXIV) (ref. 217).

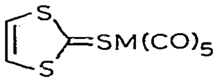


LXXXIV

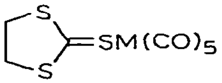
Methyl iodide adds to $CpMo(CO)(NCMe)_2^-$ to produce, through isocyanide insertions, an imino-dimethylamino carbene unit, i.e., $CpMo(CO)I(Me_2N-C-C(Me)-NMe)$, whereas $CpMo(CO)_2(NCMe)^-$ can have only one insertion thus yielding $CpMo(CO)_2(CNMe_2)$ in which the MeN=CMe group is proposed to be a 3-electron donor (ref. 218). The analogous tungsten complex, $CpW(CO)_2(CNMe)^-$ yields $CpW(Me)(CO)_2(CNMe)$ without insertion (ref. 218). Attempts to prepare di- or tridentate ligates from cyclic trithiones by replacing the diene or triene from (bicyclo-[2.2.1]heptadiene)-$M(CO)_4$ (M=Cr, Mo) or (cycloheptatriene)$Mo(CO)_3$ resulted in carbonyl abstraction and the preparation of $LM(CO)_5$ derivatives such as LXXXV, LXXXVI, and LXXXVII (ref. 219).


M = Mo

LXXXV


M = Cr, Mo

LXXXVI


M = Cr, Mo

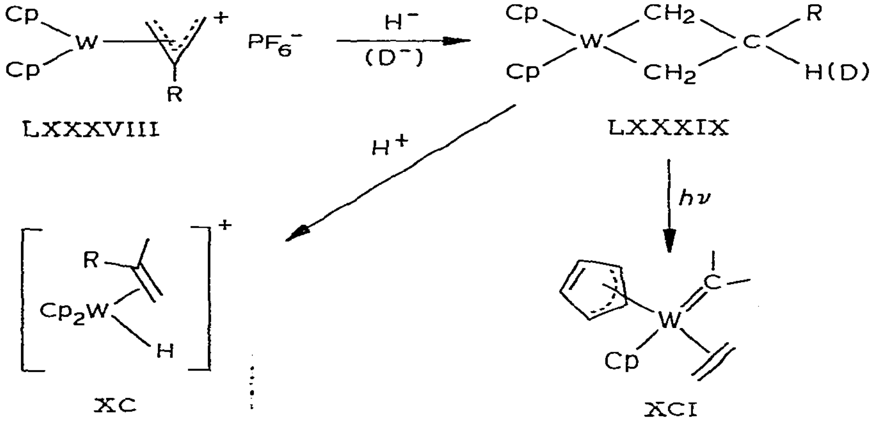
LXXXVII

ORGANIC SYNTHESIS AND CATALYSIS

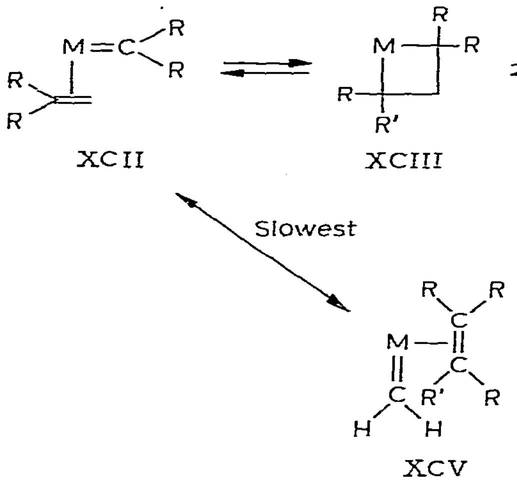
Molybdenum hexacarbonyl, but not $W(CO)_6$ or $Cr(CO)_6$ under the same conditions, acts as a deoxygenation agent as well as catalyzes the formation of thioacetals from α-bromosulfoxides (ref. 220). Catalytic properties of: $H_2[Mo_2O_4(OH)_2(H_2O)_2]\cdot 3H_2O$, $Mo(CO)_6$, $MoO_2(acac)_2$, $MoO(OH)_3(t\text{-}C_6H_{11}O_2)_2$ and Mo(V)acetylacetonate in the epoxidation run of cyclohexene with cumene hydroperoxide were examined (ref. 221). Kinetic studies for the model reaction at a molar ratio of cyclohexene: cumene hydroperoxide:Mo catalyst=1:1:0.002 at 85°C and 90°C in nitrobenzene and benzene were examined (ref. 221). $H_2[Mo_2O_4(OH)_2(H_2O)_2]\cdot H_2O$ shows highest catalytic selectivity due to its electronic structure (ref. 221). A 1:4 mixture of PhLi and WCl_6 arylates ethers and tertiary amines at the α position (ref. 222). E.g., Et_2O gave 80% EtOCHPhMe and Et_3N gave 35% Et_2-NCHPhMe (ref. 22). No reaction was observed with sulfides and phosphines (ref. 222). The photochemical preparation of $Cr(CNAr)_5$(olefin) from $Cr(CNAr)_6$, where Ar=phenyl, p-tolyl, p-anisyl; olefin=fumaronitrile, dimethylfumarate, and maleic anhydride, was described (ref. 223). The weak electron acceptor acrylonitrile was unreactive under the conditions used for the synthesis whereas the strong electron acceptor tetracyanoethylene needs no illumination to effect reaction (ref. 223).

The condensation of norbornene to isomeric mixtures of dimers and small amounts of trimers was catalyzed by WCl_6, $MoCl_5$ and $ReCl_5$ (ref. 224). The catalysts were activated by trace amounts of water but inactivated by n-BuLi (ref. 224). Metal hydrides as well as metallocyclobutanes were suggested as intermediates (ref. 224). Alumina- or silicon dioxide-adsorbed $Mo(CO)_6$ has been shown to reversibly lose CO, beginning at -20°C (ref. 225). IR evidence suggests existence of species such as C_{4v} $Mo(CO)_5$, $Mo(CO)_5L$ (L=OH group from alimina surface), and two or three stable subcarbonyls, $Mo(CO)_x$ (ref. 225). Interestingly, exposure of the stable sub-carbonyls to ^{13}CO apparently give only $Mo(^{13}CO)_x$ and no mixed $^{13}CO^{12}CO$ species (ref. 225). The reduction of cyclopropene to cyclopropane and propene was found to be a good chemical probe of the Fe-Mo nitrogenase protein (ref. 226). Molybdenum sulfide acts as a hydrogenation catalyst for alkenes and dienes and in the process conserves the molecularity of H_2 or D_2, purportedly via Mo-alkyl intermediates (ref. 227). Further work on this system showed that hydrogenation of butadiene with HD led to formation of a mixture of [3-D_1]- and [4-D_1]-but-1-ene, whose ratio agrees with the kinetic isotope effect expected for isobutenyl-Mo-sulfide-surface intermediates (ref. 228). A study of the effectiveness of cyclopentadienylsodium and phenylethynylsodium as cocatalysts with WCl_6 for the metathesis of 2-heptene indicated that a wide range of optimum mole ratios of RM to WCl_6 was possible with these cocatalysts (ref. 229). In addition, the new catalyst systems purportedly maintained activity and were less apt to be poisoned than their n-BuLi/WCl_6 counterparts, for example (ref. 229). The isomerization of <u>cis</u>-pent-2-ene that accompanies "non-productive" metathesis at low conversions was studied by Basset, et. al., using the catalysts $W(CO)_5PPh_3$ and $W(CO)_5P(OPh)_3$ with $EtAlCl_2$ and O_2 as co-catalysts, as well as the $WCl_6/SnMe_4$ catalyst system (ref. 230). All gave ratios of <u>ca.</u> 0.8 for trans-C_4/cis-C_4 product distribution and of <u>ca.</u> 3 for the trans-C_5/trans-C_4 isomerization ratio (ref. 230). Diphenylcarbenetungstenpentacarbonyl is also an effective metathesis catalyst for 1-methyl-transcyclooctene, yielding a perfectly alternating polymer [poly(1-methyl-1-octene-1,8-diyl)] (ref. 231). Quantitative UV spectroscopy indicated one diphenylethene group per average polymer unit; i.e., the metathesis generator is at the ends of the polymer chain (ref. 231). Quite to the contrary regarding the generally observed selectivity preference of olefin metathesis catalysts towards internal olefin metathesis, Farona and Motz found that the $Mo(CO)_5(pyridine)Me_3Al_2Cl_3R_4NCl$ catalyst system produced only products of terminal metathesis (ref. 232). Thus, ethylene, dec-5-ene and totally recovered hex-2-ene were obtained from attempts to cross metathesize hex-1-ene and hex-2-ene (ref. 232). Evidence for the solvent-dependent formation of an initiating and propagating metal-coordinated carbene was given (ref. 232). The importance of trace amounts of oxygen for the activity of olefin metathesis catalysts such as WCl_6/RM (RM=$EtAlCl_2$, $ZnMe_2$ or BuLi) was reported (ref. 233). In the same study $WOCl_4/EtAlCl_2$ was found to be a catalyst of high activity towards internal acyclic olefins with or without rigorous exclusion of air (ref. 233). A new, nicely homogeneous, catalyst system $W(OMe)_6/EtAlCl_2$ was used to illustrate the need for both O and Cl in these W(VI) based catalysts (ref. 233). The reaction of $MoCl_2(NO)_2L_2$ (L=Py and PPh_3) and $MoCl_3(NO)(OPPh_3)_2$ with $C_2H_5AlCl_2$, $AlCl_3$ and $Al(C_2H_5)_3$ under both argon and carbon monoxide has been followed by I.R. spectroscopy (ref. 234). Results from this study have been employed in discerning the nature of the catalytic activity of these complexes in olefin metathesis (ref. 234).

Some of the most exciting work in the VIB metal chemistry to be published in 1976 was in regard to the mechanism of olefin metathesis. Earlier views of a pair-wise scrambling of olefins have generally gone unsupported and the carbene-metallocyclobutane chain mechanism has emerged with stronger support for many catalyst systems. A useful review of the mechanistic aspects of olefin metathesis was published by Calderon, et. al. (ref. 235). Appropriate to the proposed metallocyclobutane intermediates in the olefin metathesis reaction was the report of the synthesis of the η^3-allylic salt $[Cp_2W(CH_2CRCH_2)]^+PF_6^-$ (LXXXVIII) which was found to react with $NaBH_4$ (or $NaBD_4$) or $NaAlH_2(OR)_2$ to give metallocyclobutane derivatives (LXXXIX) (ref. 236). Acidification yielded the hydrido-olefin complex cation, (XC). Whereas thermal decomposition of (LXXXIX) (R=H) produces cyclopropane and propene, photochemical decomposition in hexane yields $CH_2=CH_2$ and CH_4 (ref. 237). The photochemical conversion of η^5-C_5H_5 to η^3-C_5H_5 producing a 16-electron intermediate purportedly promotes conversion of the metallocycle to the olefin-carbene complex, (XCI) (ref. 237).



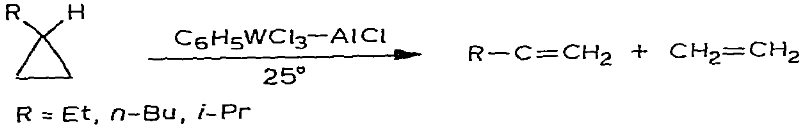
Further definitive work supporting the non-pairwise exchange of alkylidene units via the carbene/metallocycle equilibrium (equation 20 and 21) in the olefin metathesis reaction was published in 1976. The selectivity of equation 20 over equation 21 was measured for several catalyst preparations including $Mo[PPh_3]_2Cl_2(NO)$ + $Me_3Al_2Cl_3$, $W(CO)_5CPh_2$, WCl_6 + nBuLi, WCl_6 + Ph_3SnEt, and WCl_6 + EtOH-$EtAlCl_2$, utilizing 1-octene-1-d_2 and 1-hexene. In all cases simple isotopic exchange between olefins was favored. Higher selectivity was observed for those tungsten catalysts which are less effective for, or slower towards, "conventional" or productive metathesis of terminal olefins (ref. 238). In a related study Muetterties and coworkers pointed out that interpretation of product ratios in the metathesis of terminal olefins should be approached with caution in view of the generally unknown nature of the active species in the WCl_6-based catalyst recipes (ref. 241). Those authors discuss the importance of synthesizing and comparing rearrangements of the various possible metallocyclobutane intermediates XCIII.



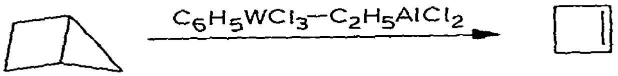
(20)

(21)

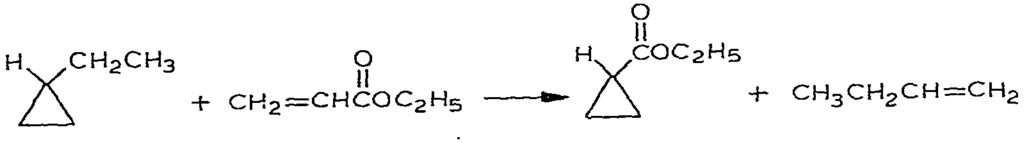
Olefin competition experiments utilizing $W(CO)_5C(C_6H_4Me)_2$ as the metathesis catalyst were used to suggest that relative reactivities depend on the stability of the initially formed olefin complex (XCII) (1-pentene >isobutylene >cis-2-butene>> 2-methyl-2-hexene) as well as the relative ease of M-carbene formation (XCII>> XCIII or XCIV) (ref. 239). Experiments which would test the extent of translational invariance in polymers of 1-methylcyclobutene as catalyzed by $W(CO)_5CPh_2$ were reported by Katz and coworkers (ref. 240). The polyisoprene thus obtained analyzes to ca. 85% Z or cis formation but occasional units (1 in 10) of 2-butene and 2,3-dimethyl-2-butene occur in the polymers (ref. 240). Two separate analyses of the appearance of ethylene-d_4, -d_2, and -d_0 from 1:1 mixtures of 2,2'-divinyl-diphenyl-d_4 and 2,2'-divinylbiphenyl, (ref. 242) and from mixtures of 1,7-octadiene and 1,7-octadiene-1,1,8,8-d_4, (ref. 245) in the presence of various Mo- and W- based catalyst systems, were also supportive of the carbene chain mechanism (ref. 243). Crucial to the carbene chain mechanism is the origin of the carbene complex in systems where he catalyst is not itself a carbene complex. The work reported by Gassman and ohnson addresses this problem (ref. 244). The catalytic activity of $PhWCl_3$/-lCl_3 towards the metathesis of cis-2-butene is effectively quenched in the resence of Michael acceptors such as ethyl acrylate, diethyl fumarate, etc. (ref. 244). The implication is that metal-alkylidene units are trapped by these electron deficient olefins, however, only small amounts of cyclopropanes were detectable in the reactions. In a related study it was shown that simple cyclopropanes react with the catalyst system according to "retrocarbene" addition, as illustrated in equations 22 and 23 (ref. 245). Cross metathesis of ethylcyclopropane and various α-β-unsaturated esters or nitriles (equation 24) was also observed by these workers (ref. 246).



(22)

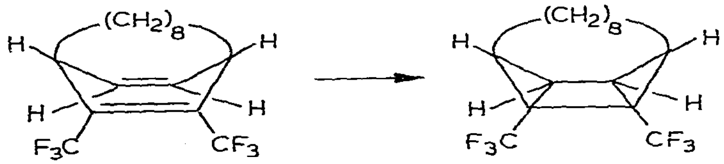


(23)



(24)

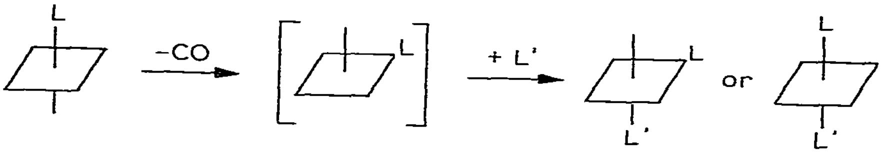
The quantitative formation of a strained polycyclic ring system from a bicyclic structure in the presence of the metathesis catalyst illustrated in equation 25 recalled the "quasi-cyclobutane" transition state for olefin metathesis (ref. 247).



(25)

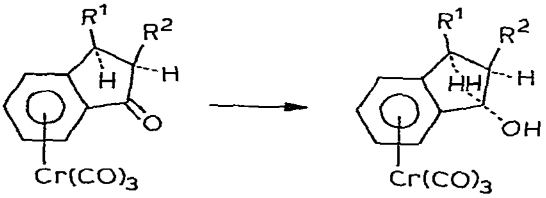
KINETICS AND MECHANISMS

Rates of CO or L dissociation from VIB metal carbonyls and derivatives were included in a review which forwarded a "cis labilization theory", or transition state site preference model, to account for large differences in rates (ref. 248). That is, a better cis labilizing ligand promotes loss of CO due to its preferential occupancy (thus lowering the transition state relative to CO or another poorer labilizing ligand) of a basal site in a square pyramidal (equation 26), or an axial site in a trigonal bipyramidal, transition state species (ref. 248).



(26)

Studies of the rates of reaction of the Group VIB metal hexacarbonyls (M=Cr, Mo, W) with benzylamine, cyclohexylamine and aniline (amine) support a rate law, $-d[M(CO)_6]/dt = k_1[M(CO)_6] + k_2[M(CO)_6][amine]$ (ref. 249). The rate law is suggestive of two competing mechanisms, with the amine-independent path involving rate-determining dissociation of CO followed by amine uptake. Activation parameters for reaction of $Mo(CO)_6$ with benzylamine, and the relative insensitivity of the rate to the identity of a wide variety of incoming nucleophiles for the amine-dependent path support a mechanism (I_d), in which M-CO bond breaking is very important (ref. 249). The mode whereby a hydride reagent labilizes CO groups was suggested by Darensbourg and Walker to possibly involve a specific hydride, μ-$H[Cr(CO)_5]_2^-$ in the case of the synthesis of $P_2Cr(CO)_4$ from $NaBH_4/Cr(CO)_6/P$ (ref. 250). Kinetic investigations of the thermal reaction of μ-$H[Cr(CO)_5]_2^-$ with PPh_3 were consistent with CO loss and substitution by P on the intact dimer prior to cleavage of the dimer (ref. 250). A work describing ^{13}CO incorporation into $Cr(CO)_4(L\text{-}L)$, where L-L = O-phen, bipy, dppe, and dppl, lent further support to Brown's cis labilization theory (ref. 251). Evidence based on amine substitution reactions in $W(CO)_4(tmpa)$(tmpa=N,N,N',N'-tetramethyl-1,3-diaminopropane) and cis-$(C_5H_{10}NH)(PPh_3)W(CO)_4$ with PPh_3 and ^{13}CO indicates (a) that the square pyramidal $[W(CO)_4PPh_3]$ intermediate arising from amine dissociation is fluxional, and (b) that the intermediate containing PPh_3 in the equatorial plane of the square pyramid is thermodynamically more stable than that containing PPh_3 in the axial position (ref 252). The characterization of the first bona fide reaction intermediate for a system in which the ring-opening mechanism is to be inferred from kinetic data derived from studies of substitution reactions of 2,2,8,8-tetramethyl-3, 7-dithianonane-tetracarbonyltungsten(0) (ref 253). The kinetics of the formation and decomposition of the intermediate have also been investigated, and the observations constitute conclusive evidence for the operation of the ring-opening mechanism (ref. 253). The oxidation of cis-$Mo(CO)_2(dmpe)_2(dmpe=Me_2PCH_2CH_2PMe_2)$ has been studied by Connor and Riley (ref. 254). With Me_3CI, the hydride, $[MoH(CO)_2(dmpe)_2]I$ and 2-methylpropene is observed; with $PhCH_2Br$, CCl_4 and Ph_3CCl, cis-$[MoX(CO)_2(dmpe)_2]X$ and R-R are produced (ref. 254). A subsequent mechanistic study showed that paramagnetic cis-$Mo(CO)_2(dmpe)_2^+$ and RX^- were the first-formed species for the latter reactions. Rapid rearrangement of the cis-Mo(I) complex to the trans isomer occurs concurrently with the formation of R· and X^-. Subsequent attack by RX on [trans-$Mo(CO)_2(dmpe)_2]X$ leads to the observed 7-coordinate product (ref. 255). The kinetics of isomerization of trans-$Mo(CO)_2(dppe)_2$-(XCVI) and trans-$W(CO)_2(dppe)_2$(XCVII), were determined from cyclic voltammetric measurements with a vitreous C electrode in organic solvents (ref. 256). The isomerizations proceed by a chelate bond-rupture mechanism with rate constants of 0.11 ± 0.006 sec^{-1} for XCVI at 25°C and 0.09 ± 0.02 sec^{-1} for XCVII at 20°C (ref. 256). Intrepretation of the large variation of kinetic isotope effect k_H/k_D, for the reaction described by equation 27 was according to a transition state resembling reactant more than product such that steric hindrance by the substituents greatly influences the reaction course (ref. 257).

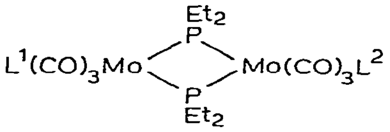


(27)

The iodination of $CpMo(CO)_3SnR_3$, $(C_5H_4Me)Mo(CO)_3SnPh_3$, other group IV derivatives of transition metal organics was kinetically investigated (ref. 258). The kinetics were studied of the reaction $Mo(CO)_3(SnMe_3)$, with Br_2 in CCl_4 and I_2 in various solvents (ref. 259). Br_2 is ∿4000 times more reactive than I_2. The reaction is akin to an aromatic substitution, the proposed mechanism involves an intermediate complex that is stabilized by vertical hyperconjugation (ref. 259). A kinetic and isotopic tracer study of the reaction described by equation 28 leads the authors to suggest that an initial bimolecular halogen abstraction reaction produces $CrCl^{2+}$ and the intermediate $(CrCHCl)^{2+}$ which rapidly exchanges with Cr^{2+} via the chloromethylene bridged intermediate $(Cr_2CHCl)^{4+}$ (ref. 260).

$$CrCHCl_2^{2+} + Cr^{2+} \xrightarrow{HClO_4} CrCH_2Cl^{2+} + Cr^{3+} + CrCl^{2+} \qquad (28)$$

The kinetics were studied of the reaction of di-μ-(diethylphosphido) bis(tetracarbonylmolybdenum)(Mo-Mo-)(I) with PBu_3 in decalin (XCII) (ref. 261). In the absence of light, it undergoes a 2-step CO substitution reaction to give the products (L^1=PBu_3, L^2=CO) and (L^1=L^2=PBu_3). The reaction does not go to completion in the presence of CO; the kinetics were studied of the forward and reverse reactions for each step. All the substitutions occur by a dissociative mechanism involving a reactive intermediate which has a coordinatively unsaturated 6-coordinate Mo atom. This coordinately unsaturated metal center shows an unexpectedly high sensitivity to the nature of the incoming ligand, and to steric and/or electronic variations on the adjacent metal atom (ref. 261).



XCII

PHYSICAL STUDIES

Vibration Studies

The correlation of ^{12}CO and ^{13}CO frequency and intensity data has been used quite successfully in determining the structure of matrix isolated metal carbonyl fragments (ref. 262). The fortuitous cancellation of terms which allows assignment of frequencies using the CO-factored force field for ^{13}CO isotopic labelled fragments that is responsible for the good fit using IR-active, but not Raman-active, modes was reiterated by Burdett, Perutz, Poliakoff, and Turner (ref. 262). In a preceding paper, Jones presented calculations to show that the same CO-factored force fields yield frequency positions in considerable error for $^{12}C^{18}O$ data (ref. 263). A complete normal coordinate analysis was performed on $M(CO)_5CS$ (M=Cr, W) and trans-$W(CO)_4(^{13}CO)(CS)$ by Butler and coworkers (ref. 264). Significantly, the equatorial CO force constants are unaffected on substitution of CS for CO in $M(CO)_6$, but the carbonyl trans to the CS has a larger CO force constant but a smaller M-C(O) force constant (ref. 264). The stronger π-acceptor capacity of CS over that of CO is also reflected in the larger M-C(S) force constant (ref. 264). The Raman spectra of mixed crystals of the group VIB metal hexacarbonyls have been described by Dariuki and Kettle (ref. 265). These spectra show an averaging of spectral features in the ν(CO) region for molecular e_g modes but a superposition for the a_{1g} modes. This observation was correlated with the absence of factor group splitting in the a_{1g} case (ref. 265). The vibrational spectrum of $CpW(CO)_3R$ (R=H, CD_3, C_2H_5 and η^1-C_3H_5) has been assigned using the local symmetries C_{5v} for the Cp ring, C_{3v} for the Cp-$W(CO)_3$ vibrations, and C_{3v} for the W-C and C-O modes (ref. 266). The

IR and Raman spectra are given, along with proposed vibrational assignments. While the local symmetry of C_{5v} does serve as an acceptable approximation for assignment of the Cp modes, there are definite examples for most of the compounds where the C_{5v} selection rules are violated, indicating the approximate nature of the local-symmetry approach (ref. 266).

Electronic Studies

The electronic spectra of a series of arenechromium tricarbonyl and dicarbonyltriphenylphosphine derivatives have been reported and their photodecay processes investigated employing visible light (ref. 267). The spectroscopic properties of mixtures of Cp_2MH_2 (M=Mo, W) and π-acidic olefins such as maleic anhydride or fumaronitrile were recorded in various solvents and found to be consistent with formation of charge transfer complexes. Indeed the $Cp_2MH_2^+$ species was reportedly formed by addition of TCNE to Cp_2MH_2 (ref. 268).

Nuclear Magnetic Resonance

Some thirty substituted η^6-(tricarbonylchromium)benzenes, including some crowded alkylsubstituted complexes, e.g. (1',1'-diethylpropyl)-, 1'-t-butyl-2',2'-dimethylpropyl)-, 1,2-di-t-butyl- and 1,2,4-tri-t-butyl-η^6-(tricarbonylchromium)benzenes were prepared (ref. 269). ^{1}H NMR spectra were recorded from acetone solutions of the complexes (ref. 269). Using the chemical shift increments of the aromatic protons on complex formation of C_6H_5CH-t-Bu_2 and a reference for the eclipsed conformation with the substituent staggered with respect to the carbonyl ligands, the contribution of this conformer to the conformational equilibrium of the other monoalkylsubstituted complexes was estimated (ref. 269). The proton NMR spectra of a number of alkyl and X (X=F, Cl, NR_2, CF_3 OR) substituted bis(arene)chromium(0) complexes were recorded on a 100 MHz instrument and assignments made (ref. 270). A dramatic reduction in J_{H-H} and J_{H-F} in the complexed arenes as compared to the free arenes was noted (ref. 270). Band-shape fitting studies for the NMR spectra of the chelate-ring methylene protons of deuterated analogs of PdX_2L and $M(CO)_4L$ (X=Cl, Br; M=Cr, Mo, W; L=$(Me_2CHSeCH_2)_2$] showed that the coalescence phenomenon observed in the temperature-dependent NMR spectra resulted from inversion of configuration about the ligand atoms and not from reversal of the chelate ring (ref. 271). Thermodynamic activation parameters for the inversion process were determined (ref. 271).

A ^{13}C NMR study of substituted biphenyl- and diphenylmethane-, diphenylethane-, cis-stilbene- and benzophenonetricarbonylchromium complexes has been reported by Brown and coworkers (ref. 272). The ^{13}C NMR chemical shifts of the ring carbons directly complexed to chromium were moved about 35 ppm upfield relative to the free ligand, whereas those not complexed underwent only small changes (1-2 ppm) (ref. 272). Carbon-13 NMR measurements were taken on an extensive list of bis(arene)chromium(0) complexes, prepared by the metal atom/vapor synthesis technique (ref. 273). Analysis of the data led the authors to conclude that complexation of the arene essentially quenches delocalization of the π-electron system. The failure of the compounds to undergo electrophilic aromatic subsitution is apparently due to the reduction of aromaticity (ref. 273). Paramagnetic metallocenes bearing n-butyl groups as substituents, (n-$BuC_5H_4)_2M$ (M=Cr, Co, Ni, V), were synthesized in order to study C-C hyperconjugation effects (ref. 274). The ^{13}C chemical shifts of the carbons β to the Cp ring were greatly influenced by the unpaired electron (ref. 274). The ^{13}C and ^1H NMR spectra are reported and interpreted for several paramagnetic metallocene species, including chromocene (ref. 275). Dimethyltetrakis(diethylamido)-ditungsten may be prepared by reaction of $W_2Cl_2(NEt_2)_4$ with MeLi (ref. 276). Carbon-13 NMR data were used to determine that the interconversion of gauche and anti forms of the complex has an activation energy of about 21 kcal mol^{-1} (ref. 276). Milbrath and Verkade report the first examples of $^1J^{95,97}{}_{Mo}{}^{31}P$ couplings for ten $(OC)_5MoL$ complexes (ref. 277). ^1H-[^{183}W], ^1H-[^{31}P], and ^1H-[^{183}W, ^{31}P] nuclear magnetic double and triple resonance experiments on 35 W complexes with tertiary phosphine, Cp, and other ligands were determined and used to design ^{183}W chemical shifts and magnetic shieldings (ref. 278).

Theoretical

An experimental estimate of σ- and π-bonding in $Cr(CO)_6$ was provided by an x-ray and neutron diffraction study of charge density (ref. 279). In this work the following charges were assigned: Cr, 0.15±.12; C, 0.09±.12; C, 0.09±.05; and O, -0.12±.05. The σ and π electron transfers are thus assumed to be nearly equal; about 0.4 electron per CO is estimated (ref. 279). The hypothetical $CrH_6{}^{6-}$ was compared with $Cr(CO)_6$ in extended Hückel calculations in order to separate the effects of σ and π bonding on stabilities of trigonal prism _vs._ octahedral geometries in six-coordinate complexes (ref. 280). Extended Hückel parameters were also used to compare calculated and observed Mo-Mo distances in $Mo_2(CO)_{10}{}^{=}$ (ref. 281). Ionization potentials as calculated by an INDO molecular-orbital method for $Cr(CO)_6$ and other simple carbonyls were in good agreement with PES data (ref. 282). Binding energies of core electrons in $Cr(C_6H_6)_2$, $C_6H_6Cr(CO)_3$, and $Cr(CO)_6$ could be obtained in the solid phase using x-ray photoelectron spectroscopy by calibrating the binding energy of a valence band observed on the solid with that of a valence band observed in the gaseous phase via ultraviolet PES (ref. 283). Correlation of the Fenske method of approximate molecular orbital calculations and He I photoelectron spectra of $Cr(CO)_5CS$, $W(CO)_5CS$ and $CpMn(CO)_2CS$ suggested that the ionizations due to the CS ligand are around 8 eV, considerably removed in energy (lower) from that of CO (ref. 284). The better π-accepting ability of CS over CO as well as the stronger interaction of occupied σ and π CS levels with metal help explain the observations (ref. 284). Results of a theoretical study on triple decker sandwich organometallics such as Cp_3M_2 led Hoffman and coworkers to suggest that $Cr_2(CO)_9$, containing 3 bridging CO groups, might be observable in matrix isolation experiments (ref. 285). Calculations of charge distribution and molecular orbital levels were used to discuss carbonyl vs. carbene or acyl carbon sites of nucleophilic attack on $(CO)_5CrC(OMe)Me$ and $(CO)_5MnC(=O)Me$ (ref. 286). The theoretical results best correlate with chemical observations if nucleophilic attack is frontier and LUMO controlled rather than charge controlled (ref. 286).

Extended Hückel molecular orbital calculations were used to rationalize the enhancement of non-planarity on complexation of cyclohexadienyl derivatives to metal carbonyl moities, $Fe(CO)_3{}^+$, $Mn(CO)_3$, and $Cr(CO)_3{}^-$ (ref. 287). Secondary antibonding repulsions between the metal and the lower methylene hydrogen in C_6H_7, evident in these calculations, are not expected to be as prominent in cyclooctatrienyl or cycloheptatrienyl complexes of $M(CO)_3$, M=Cr, Mo, W (ref. 287). The effect of substitution on the aromatic ring in arene-chromium tricarbonyl derivatives has been studied by ESCA (ref. 288). The chemical shifts of the core ionization energies (C 1s, O 1s, Cr 3s) of these derivatives were measured and information on the bonding in these complexes was obtained (ref. 288). INDO calculations on the cations $[(C_7H_6X)Cr(CO)_3]^+$ (X=H, OMe, COOMe) reveal an increase in positive charge on the $C_7H_7{}^+$ ion upon coordination to $Cr(CO)_3$ although there is a decrease in reactivity towards nucleophiles (ref. 299). This was explained in terms of increased bond index values in the $C_7H_7{}^+$ or related ion upon binding to the metal and it was concluded that the site of nucleophilic attack in $[(C_7H_7X)Cr(CO)_3]^+$ does not in general correlate with any specific electronic parameter (ref. 289). The complexes Cp_2MoCO, Cp_2MoCl_2, Cp_2MoD_2, $Cp_2MoCl_2{}^+$, and $Cp_2Mo(CO)R$ were among those discussed in a theoretical paper dealing with correlating the extent of distortion in Cp_2M fragments with electronic structure (ref. 290). This paper includes a rationale for facile olefin insertion into M-H or M-R bonds of species such as Cp_2ZrClH. Cp_2TiClR or $Cp_2Ti(C_2H_4)H^+$ vs. the inactivity of $Cp_2Mo(C_2H_4)H^+$ or $Cp_2Nb(C_2H_4)H$ (ref. 290). A molecular-orbital study of the ground and excited-state properties of metallocenes of the first-row transition metal ions, including $Cr(Cp)_2{}^+$, has been reported (ref. 291).

Miscellaneous Physical Studies

Heats of reactions have been determined for $W(CO)_{6-n}(CH_3CN)_n + nCO \rightarrow W(CO)_6 + n(CH_3CN)$(n=1,2,3) (ref. 292). Combining this data with measured heat capacities and sublimation energies and knowing standard enthalpies of formation for $W(CO)_6$, CO, and CH_3CN, the standard enthalpies of formation of each member of the series, $W(CO)_{6-n}(CH_3CN)_n$ is afforded. W-acetonitrile bond energies were derived to be 45 kcal/mole which is comparable to the bond energy of a W-carbonyl bond (ref. 292). Differential scanning calorimetry techniques were utilized in the study of the melting of group VI transition metal hexacarbonyls in sealed, evacuated ampoules (ref. 293). Resulting thermodynamic parameters:

$Cr(CO)_6$: $\Delta H° = 5.6 \pm 0.1$ kcal mole^{-1}
$\Delta S° = 13.2$ cal°C^{-1} mole^{-1}
(m.p. = 150 ± 2°C)
$Mo(CO)_6$: $\Delta H° + 6.4 \pm 0.1$ kcal mole^{-1}
$\Delta S° = 15.3$ cal°C^{-1} mole^{-1}
(m.p. 146 ± 2°C)
$W(CO)_6$: $\Delta H° = 6.5 \pm 0.1$ kcal mole^{-1}
$\Delta S° + 14.8$ cal°C^{-1} mole^{-1}
(m.p. = 166 ± 2°C)

Combining these values with reported sublimation data, enthalpies of vaporization were calculated (ref. 293). Having obtained these new values and knowing the reported sublimation parameters, phase diagrams for solid-gas and liquid-gas were obtained. From these diagrams calculations for boiling points of $Mo(CO)_6$ and $W(CO)_6$ were 160.8 and 184.2°C, respectively (ref. 293). Domrachev and Zinov'ev have carried out thermodynamic studies of the equilibrium in the direct-synthesis reaction of dibenzenechromium from benzene and chromium (ref. 294). The heat of formation of WMe_6 (73(kJ/mole) as determined from measurements on its heat of hydrolysis was used to estimate the average W-Me bond enthalpy, 159 ± 7 kJ/mole, or 62 ± 2 kcal/mole (ref. 295). It was stressed that correlation of the enthalpy of formation with the observed thermal stability was unwarranted in view of alternate methods of thermal decomposition such as hydride transfer (ref. 295). Cyclic-voltammetry was used to study the reduction of $Cr(CO)_6$ to $[Cr_2(CO)_{10}]^{2-}$ at a Pt electrode in MeCN (ref. 296). Cyclic voltammetry studies of dicarbene complexes of Mo and W such as $(imid)_2M(CO)_4$ (imid=1,3-dimethyl-4-imidazolin-2-ylidene) showed that both cis and trans isomers displayed a reversible wave at identically the same potential (ref. 297). The trans complexes however displayed an additional irreversible wave at more negative potentials; this was proposed to result from (in the oxidative process) production of trans$^+$ which rapidly isomerizes to cis$^+$ (ref. 297). The usefulness of electrochemical studies in elucidating the chemistry of metal carbonyl derivatives was further shown in a report regarding $Cr(CO)_5I$ (ref. 298). Iodochromium pentacarbonyl was prepared from $Et_4N^+Cr(CO)_5I^-$ by $KMnO_4$ oxidation in acetone. The resultant blue solutions were stable at -78° but disproportionated at higher temperatures. Triphenylphosphine was readily oxidized by $Cr(CO)_5I$ yielding Ph_3PO and $Cr(CO)_5I^-$ (ref. 298). Vibrational, ^{13}C NMR, electronic absorption, and photoelectron spectra of the complexes $W(CO)_5$(4R-pyridine) are discussed in terms of the influence of variation of R on the trans carbonyl and the extent of π-bonding between tungsten and the py ligand (ref. 299). Enthalpies are determined for the following reaction

$$W(CO)_5(4R\text{-}Py)(s) + CO(g) \rightarrow W(CO)_6(g) + 4\text{-}R\text{-}Py(g) \qquad (29)$$

The decrease in reaction enthalpy in going from R=CH_3 to R=CN is due to a weakening of W-py bond (ref. 299). Analysis of the electron spin resonance spectrum of the radical anion, $[Ph(MeO)CCr(CO)_5]^{\dot{-}}$ formed by reducing the neutral carbene complex with Na/K, indicated localization of the unpaired electron on the carbene moiety, and the Ph ring to be coplanar with the Cr-$C_{carbene}$-O plane as well as fixed on the esr time scale (ref. 300). Similar studies on other metal carbene complexes utilizing various one-electron reducing agents, sodium naphthalide, $Mn(CO)_5$, $CpFe(CO)_2^-$, CH_2PPh_3, PhLi and t-BuLi, were also reported (ref. 300). The magnetic susceptibility of chromocene has been measured between 83 and 293°K and the data are supportive of a $3\Delta(\sigma\delta^3)$ ground state (ref. 301). The fragmentation of η^6-thiophenechromium tricarbonyl under electron impact was studied (ref. 302). The formation of the rearrangement ion CrS^+ was observed (ref. 302). The use of radiochemistry in the preparation of organometallics was reported (ref. 303). Thus $[CpMo(CO)_3]_2$ containing ^{99}Mo undergoes β- decay producing 74.4% $CpTc(CO)_3$ containing ^{99m}Tc, and $^{99}Mo(CO)_6$ yields 73.5% of $^{99m}Tc(CO)_5$. Some $^{99m}Tc(CO)_5$ is also found in the former process (ref. 303).

Crystal Structures

Crystal structures of the following compounds were reported: bis(2,6-dimethylpyridine)chromium, (ref. 304) dicarbonyl-η^5-cyclopentadienyl[(3-dimethylarsino)propyl]molybdenum, (ref. 305) bis(2,6-dimethylpyridine)chromium, (ref. 306) trans-oxochlorotetrakis(methylisocyanide)molybdenum(IV)triiodide, (ref. 307) 1,1-dimethoxy-2,4,6-triphenyl-λ^5-phosphorin-chromiumtricarbonyl and 4-tert-butyl-1,1-di-fluoro-2,6-diphenyl-λ-phosphorinchromiumtricarbonyl, (ref. 308) 1:2 addition complex of tricarbonylmesitylenemolybdenum with mercury(II) chloride, (ref. 309) hexakis(trimethylsilymethyl)ditungsten, (ref. 310) trans,trans-$[Cr(I)(CO)_2(PPh_2Me)_2NO)]$, (ref. 311) areneolefindicarbonylchromium chelate complex with (2,5-dimethylbenzyl)allyl ether as the chelate ligand, (ref. 312) carbonylcyclopentadienylhexafluorobut-2-yne-(pentafluorophenylthio)molybdenum, cyclopentadienyl(hexafluorobut-2-yne)oxo(pentafluorophenylthio)molybdenum, (ref. 313) and the iodo-bridged complex μ-$I_2W_2(CO)_8$ (ref. 314).

References

1. I. Dellien, F.M. Hall and L.G. Hepler, Chem. Rev. 76 (1976) 283-310.
2. T.H. Whitesides and R. Budnick, Inorg. Chem. 15 (1976) 874.
3. R.B. King, Coord. Chem. Rev. 20 (1976) 155-169.
4. L.H. Jones and B.I. Swanson, Acct. Chem. Res. 9 (1976) 128-134.
5. C.P. Casey and S.M. Neumann, J. Am. Chem. Soc. 98 (1976) 5395.
6. W. Beck and N. Kottmair, Chem. Ber. 109 (1976) 970.
7. P. Krausz, F. Garnier, and J.E. Dubois, J. Organomet. Chem. 108 (1976) 197.
8. G. Coudurier, P. Gallezot, H. Praliaud, M. Primet, and B. Imelik, Comp. Rend. 282C (1976) 311.
9. M.S. Wrighton, H.B. Abrahamson, and D.L. Morse, J. Am. Chem. Soc. 98 (1976) 4105.
10. A.B. Cornwell, P.G. Harrison, and J.A. Richards, J. Organomet. Chem. 108 (1976) 47.
11. J.A. Connor, J.P. Day, and R.M. Turner, J.C.S. Dalton (1976) 108.
12. J.A. Connor, J.P. Day, and R.M. Turner, J.C.S. Dalton (1976) 283.
13. T.C. DeVore, Inorg. Chem. 15 (1976) 1315.
14. P.M. Treichel and G.J. Essenmacher, Inorg. Chem. 15 (1976) 146.
15. V. Katovic, J.L. Templeton, and R.E. McCarley, J. Am. Chem. Soc. 98 (1976) 5705.
16. A. Bino, M. Ardon, I. Maor, M. Kaftory, and Z. Dori, J. Am. Chem. Soc. 98 (1976) 7093.
17. C.G. Pierpont and H.H. Downs, J. Am. Chem. Soc. 98 (1976) 4834.
18. L. Weber, Z. Naturforsch. 31b (1976) 780-785.
19. P.M. Treichel and D.B. Shaw, Inorg. Chim. Acta 16 (1976) 199-202.
20. F. Hohmann and H. TomDieck, J. Organomet. Chem. 118 (1976) C35.
21. B.D. Dombek and R.J. Angelici, Inorg. Chem. 15 (1976) 1089.
22. B.D. Dombek and R.J. Angelici, Inorg. Chem. 15 (1976) 2397.
23. B.D. Dombek and R.J. Angelici, Inorg. Chem. 15 (1976) 2403.
24. B.D. Dombek and R.J. Angelici, J. Am. Chem. Soc. 98 (1976) 4110.
25. S.S. Woodard, R.A. Jacobson, and R.J. Angelici, J. Organomet. Chem. 117 (1976) C75.
26. M. Poliakoff, Inorg. Chem. 15 (1976) 2022.

27. M. Poliakoff, Inorg. Chem. 15 (1976) 2892.
28. W. Malisch and P. Panster, Angew. Chem. Int. Ed. Engl. 15 (1976) 618.
29. P. Panster and W. Malisch, Chem. Ber. 109 (1976) 692.
30. P. Panster and W. Malisch, Chem. Ber. 109 (1976) 2112.
31. P. Panster and W. Malisch, Chem. Ber. 109 (1976) 3842.
32. C.M. Bartish and C.S. Kraihanzel, J. Organomet. Chem. 112 (1976) C31.
33. E. Lindner and W.P. Meier, Chem. Ber. 109 (1976) 3323.
34. L. Staudacher and H. Vahrenkamp, Chem. Ber. 109 (1976) 218.
35. P. Jutzi, H. Saleske, and D. Nadler, J. Organomet. Chem. 118 (1976) C8.
36. J.R. DeLerno, L.M. Trefonas, M.Y. Darensbourg, and R.J. Majeste, Inorg. Chem. 15 (1976) 816.
37. H. Schumann, J. Held, H. -J. Kroth and W. -W. duMont, Chem. Ber. 109 (1976) 246.
38. R.L. Keiter and E.W. Abel, J. Organomet. Chem. 107 (1976) 73.
39. M.L. Walker and J.L. Mills, J. Organomet. Chem. 120 (1976) 355.
40. J. Ellermann and H. Schössner, J. Organomet. Chem. 118 (1976) C69.
41. G. Huttner, H. -G. Schmid, A. Frank, and O. Orama, Angew. Chem. Int. Ed. Engl. 15 (1976) 234.
42. W.A. Schenk, J. Organomet. Chem. 117 (1976) C97.
43. M.S. Arabi, R. Mathieu, and R. Poilblanc, J. Organomet. Chem. 104 (1976) 323.
44. T. Tatsumi, H. Tominaga, M. Hidai and Y. Uchida, J. Organomet. Chem. 114 (1976) C27.
45. F. Hohmann, and H. Dieck, J. Organomet. Chem. 122 (1976) 197.
46. R.B. King, J.C. Cloyd, Jr., and R.H. Reimann, Inorg. Chem. 15 (1976) 449.
47. G.E. Graves and L.W. Houk, Inorg. Chem. 15 (1976) 7.
48. M.R. Snow, and F.L. Wimmer, Aust. J. Chem. 29 (1976) 2349.
49. P.W. Lednor, W. Beck and H.G. Fick, J. Organomet. Chem. 113 (1976) C19.
50. M. Herberhold and K. Leonhard, Angew. Chem. Int. Ed. Engl. 15 (1976) 230.
51. S.C. Tripathi, S.C. Srivastava, and R.P. Mani, J. Organomet. Chem. 105 (1976) 239.
52. M. Moll, H. Behrens, R. Kellner, H. Knöchel, and P. Würstl, Z. Naturforsch. 31b (1976) 1019.

53. M. Herberhold and M. Süss-Fink, Z. Naturforsch. 31b (1976) 1489.

54. M. Kooti and J.F. Nixon, J. Organomet. Chem. 105 (1976) 217.

55. M.H. Quick and R.J. Angelici, Inorg. Chem. 15 (1976) 160.

56. D. Sellmann, A. Brandl, and R. Endell, J. Organomet. Chem. 111 (1976) 303.

57. R. Meig, J. Kuyper, D.J. Stufkens, and K. Vrieze, J. Organomet. Chem. 110 (1976) 219.

58. M.N. Ackermann and L. -J. Kou, Inorg. Chem. 15 (1976) 1423.

59. T.E. Dorsett and R.A. Walton, J.C.S. Dalton (1976) 347.

60. T.E. Dorsett and R.A. Walton, J. Organomet. Chem. 114 (1976) 127.

61. R.B. King and C.A. Harmon, Inorg. Chem. 15 (1976) 879.

62. K. Fukushima, T. Miyamoto and Y. Sasaki, J. Organomet. Chem. 107 (1976) 265.

63. E.W. Ainscough, E.J. Birch, and M. Brodie, Inorg. Chim. Acta 20 (1976) 187.

64. E. Lindner and W.P. Meier, J. Organomet. Chem. 114 (1976) 67.

65. R.J. Cross, G. Hunter and R.C. Massey, J.C.S. Dalton (1976) 2015.

66. U. Behrens and F. Edelmann, J. Organomet. Chem. 118 (1976) C41.

67. L. Weber, J. Organomet. Chem. 105 (1976) C9.

68. M. Herberhold and G. Suss, Angew. Chem. Int. Ed. Engl. 15 (1976) 366.

69. J.K. Kouba and S.S. Wreford, Inorg. Chem. 15 (1976) 1463.

70. S.C. Tripathi, S.C. Srivastava, and A.K. Shrimal, J. Organomet. Chem. 118 (1976) 325.

71. S.C. Tripathi, S.C. Srivastava, and A.K. Shrimal, Inorg. Chim. Acta 18 (1976) 231.

72. L.H. Simons, P.E. Riley, R.E. Davis and J.J. Lagowski, J. Am. Chem. Soc. 98 (1976) 1044.

73. P.E. Riley and R.E. Davis, Inorg. Chem. 15 (1976) 2735.

74. T. -S. Tan and M.J. McGlinchey, J.C.S. Chem. Comm. (1976) 155.

75. W.B. Davies, M.L.H. Green, and A.J. Jacobson, J.C.S. Chem. Comm. (1976) 781.

76. J.A. Segal, M.L.H. Green, J. -C. Daran and K. Prout, J.C.S. Chem. Comm. (1976) 766.

77. M.J. McGlinchey and T. -Seng Tan, J. Am. Chem. Soc. 98 (1976) 2271.

78. A.N. Nesmeyanov, N.N. Zaitseva, G.A. Domrachev, V.D. Zinov'ev, L.P. Yur'eva and I.I. Tverdokhlebova, J. Organomet. Chem. 121 (1976) C52.

79. A. Gilbert, J.M. Kelley, M. Budzwait, and (the late) E.K. von Gustorf, Z. Naturforsch. 31b (1976) 1091.

80. M.F. Semmelhack, H.T. Hall, Jr., and M. Yoshifuji, J. Am. Chem. Soc. 98 (1976) 6387.

81. M. Herberhold and W. Bernhagen, Angew. Chem. Int. Ed. Engl. 15 (1976) 617.

82. F. Van Meurs and H. Van Koningsveld, J. Organomet. Chem. 118 (1976) 295.

83. F. Van Meurs, J.M.A. Baas, J.M. Van der Toorn, and H. Van Bekkum, J. Organomet. Chem. 118 (1976) 305.

84. R.D. Adams and D.F. Chodosh, J. Organomet. Chem. 120 (1976) C39.

85. F. Van Meurs, J.M.A. Baas, and H. Van Bekkum, J. Organomet. Chem. 113 (1976) 353.

86. A.P. Hagen and H.W. Beck, Inorg. Chem. 15 (1976) 1512.

87. G.M. Holtzapple, P.S. Woon, and M.F. Farona, Inorg. Nucl. Chem. Lett. 12 (1976) 623.

88. J.R. Blackborow, R. Grubbs, A. Miyashita, and A. Scrivanti, J. Organomet. Chem. 120 (1976) C49.

89. H. -G. Biedermann, K. Öfele, and J. Tajtelbaum, Z. Naturforsch. 31b (1976) 321.

90. R.S. Bly, K. -K. Tse, and R.K. Bly, J. Organomet. Chem. 117 (1976) 35.

91. M. Ashraf, Can. J. Chem. 54 (1976) 448.

92. A.M. Ciplys, R.J. Geue, and M.R. Snow, J.C.S. (1976) 35.

93. M. Lückoff and K. Dimroth, Angew. Chem. Int. Ed. Engl. 15 (1976) 503.

94. W. Siebert and R. Full, Angew. Chem. Int. Ed. Engl. 15 (1976) 45.

95. C.G. Salentine and M.F. Hawthorne, Inorg. Chem. 15 (1976) 2872.

96. B.V. Lokshin, E.B. Rusach, N.E. Kolobova, Y.V. Makarov, N.A. Ustynyuk, V.I. Zdanovich, A.Z. Zhakaeva, and V.N. Setkina, J. Organomet. Chem. 108 (1976) 353.

97. M. Pankowski, M. Bigorgne, and Y. Chauvin, J. Organomet. Chem. 110 (1976) 331.

98. J.E. Ellis, J. Organomet. Chem. 111 (1976) 331.

99. (a) R.D. Adams, Inorg. Chem. 15 (1976) 169.
(b) R.D. Adams, Inorg. Chem. 15 (1976) 174.

100. J.E. Ellis, R.A. Faltynek, and S.G. Hentges, J. Organomet. Chem. 120 (1976) 389.

101. W. Malisch and R. Alsmann, Angew. Chem. Int. Ed. Engl. 15 (1976) 769.

102. M. Herberhold and H. Alt, Liebigs Ann. Chem. (1976) 292.

103. M. Herberhold, H. Alt, and C.G. Kreiter, Liebigs Ann. Chem. (1976) 300.

104. T. Inglis and M. Kilner, J.C.S. Dalton (1976) 562.

105. J.S. Braterman, J.L. Davidson, and D.W.A. Sharp, J.C.S. Dalton (1976) 241.

106. C. Eaborn, N. Farrell, J.L. Murphy, and A. Pidcock, J.C.S. Dalton (1976) 58.

107. K.H. Pannell, J.B. Cassias, G.M. Crawford, and A. Flores, Inorg. Chem. 15 (1976) 2671.

108. C. Giannotti and G. Merle, J. Organomet. Chem. 105 (1976) 97.

109. T.A. George and C.D. Sterner, Inorg. Chem. 15 (1976) 165.

110. K. Triplett and M.D. Curtis, Inorg. Chem. 15 (1976) 431.

111. H. Brunner and J. Wachter, Angew. Chem. Int. Ed. Engl. 15 (1976) 316.

112. J. Hills, M. Ishaq, B. Gorewit, and M. Tsutsui, J. Organomet. Chem. 116 (1976) 91.

113. F.H. Köhler and G. Matsubayashi, Chem. Ber. 109 (1976) 329.

114. H. Brunner and J. Wachter, J. Organomet. Chem. 107 (1976) 307.

115. H. Brunner, W.A. Herrmann, and J. Wachter, J. Organomet. Chem. 107 (1976) C11.

116. E. Pfeiffer, J. Kuyper, and K. Vrieze, J. Organomet. Chem. 105 (1976) 371.

117. H. Brunner and J. Wachter, J. Organomet. Chem. 113 (1976) C58.

118. P. Eilbracht, J. Organomet. Chem. 120 (1976) C37.

119. P. Eilbracht, Chem. Ber. 109 (1976) 1429.

120. M. Mickiewicz, K.P. Wainwright, and S.B. Wild, J.C.S. Dalton (1976) 262.

121. J.L. Davidson, M. Green, F.G.A. Stone, and A.J. Welch, J.C.S. Dalton (1976) 738.

122. C.M. Lukehart and J.V. Zeile, J. Organomet. Chem. 105 (1976) 231.

123. M. Bockmann, M. Cooke, M. Green, H.P. Kirsch, F.G.A. Stone, and A.J. Welch, J.C.S. Chem. Comm. (1976) 381.

124. G.C. Allen, M. Green, B.J. Lee, H.P. Kirsch, and F.G.A. Stone, J.C.S. Chem. Comm. (1976) 794.

125. J.R. Blackborow, C.R. Eady, E.A. Koerner von Gustorf, A. Serivanti, and O. Wolfbeis, J. Organomet. Chem. 108 (1976) C32.

126. M.L.H. Green and R.B.A. Pardy, J. Organomet. Chem. 117 (1976) C13.

127. F.A. Cotton, P. Lahuerta and B.R. Stults, Inorg. Chem. 15 (1976) 1866.

128. F.A. Cotton and B.E. Hanson, Inorg. Chem. 15 (1976) 2806.

129. D. Mohr, H. Wienand and M.L. Ziegler, Z. Naturforsch. 31b (1976) 66.

130. E.E. Isaacs and W.A.G. Graham, J. Organomet. Chem. 120 (1976) 407.

131. D.A. Sweigart, M. Gower, and L.A.P. Kane-Maguire, J. Organomet. Chem. 108 (1976) C15.

132. G.R. John and L.A.P. Kane-Maguire, J. Organomet. Chem. 120 (1976) C45.

133. G.R. John, L.A.P. Kane-Maguire, and D.A. Sweigart, J. Organomet. Chem. 120 (1976) C47.

134. A. Salzer, Inorg. Chim. Acta 18 (1976) L31.

135. A. Salzer, Inorg. Chim. Acta 17 (1976) 221.

136. M. Djazayeri, C.G. Kreiter, H.M. Kurz, M. Lang and S. Özkar, Z. Naturforsch. 31b (1976) 1238.

137. H. Schaper and H. Behrens, J. Organomet. Chem. 113 (1976) 361.

138. H. Schaper and H. Behrens, J. Organomet. Chem. 113 (1976) 377.

139. S.C. Tripathi, S.C. Srivastava, R.D. Pandey, and R.P. Mani, J. Organomet. Chem. 110 (1976) 67.

140. G.R. John and L.A.P. Kane-McGuire, J. Organomet. Chem. 120 (1976) C45.

141. A. Salzer, J. Organomet. Chem. 107 (1976) 79.

142. R. Goddard, S.A.R. Knox, F.G.A. Stone, M.J. Winter, and P. Woodward, J.C.S. Chem. Comm. (1976) 559.

143. J. Müller, W. Holzinger and F.H. Köhler, Chem. Ber. 109 (1976) 1222.

144. J.A. Van Doorn, C. Masters, and H.C. Volger, J. Organomet. Chem. 105 (1976) 245.

145. S.C. Tripathi, S.C. Srivastava, and D.N. Pathak, J. Organomet. Chem. 107 (1976) 315.

146. R.A. Andersen, A.L. Galyer, and G. Wilkinson, Angew. Chem. Int. Ed. Engl. 15 (1976) 609.

147. J.L. Davidson, M. Green, F.G.A. Stone, and A.J. Welch, J.C.S. Dalton (1976) 738.

148. J.L. Davidson, M. Green, J.Z. Nyathi, C. Scott, F.G.A. Stone, A.J. Welch, and P. Woodward, J.C.S. Chem. Comm. (1976) 714.

149. R.D. Adams and D.F. Chodosh, J. Organomet. Chem. 122 (1976) C11.

150. J.Z. Chrzastowski and M.D. Johnson, J.C.S. Dalton (1976) 2456.

151. K.H. Pannell, M.F. Lappert, and K. Stanley, J. Organomet. Chem. 112 (1976) 37.

152. M.H. Chisholm, M. Extine, F.A. Cotton, and B.R. Stults, J. Am. Chem. Soc. 98 (1976) 4683.

153. C. Santini-Scampucci and J.G. Riess, J.C.S. Dalton (1976) 195.

154. M.R. Hyde and J.H. Espenson, J. Am. Chem. Soc. 98 (1976) 4463.

155. J.P. Leslie, II, and J.H. Espenson, J. Am. Chem. Soc. 98 (1976) 4839.

156. J.H. Espenson and G.J. Samuels, J. Organomet. Chem. 113 (1976) 143.

157. J.D. Koola and H.H. Brintzinger, J.C.S. Chem. Comm. (1976) 388.

158. M.Y. Darensbourg and C. Borman, Inorg. Chem. 15 (1976) 3121.

159. R.A. Love, H.B. Chin, T.F. Koetzle, S.W. Kirtley, B.R. Whittlesey and R. Bau, J. Am. Chem. Soc. 98 (1976) 4491.

160. W. Beck, W. Danzer, A.T. Liu, and G. Huttner, Angew. Chem. Int. Ed. Engl. 15 (1976) 495.

161. W.A. Herrmann, Chem. Ber. 109 (1976) 3489.

162. B.R. Francis, M.L.H. Green, T. Luong-thi, and G.A. Moser, J.C.S. Dalton (1976) 1339.

163. S.C. Tripathi, S.C. Srivastava, and D.N. Pathak, J. Organomet. Chem. 110 (1976) 73.

164. D.M. Allen, A. Cox, T.J. Kemp, Q. Sultana and R.B. Pitts, J.C.S. Dalton (1976) 1189.

165. M.H. Chisholm and M.W. Extine, J. Am. Chem. Soc. 98 (1976) 6393.

166. W.I. Bailey, Jr., F.A. Cotton, J.D. Jamerson, and J.R. Kolb, J. Organomet. Chem. 121 (1976) C23.

167. J. Dehand and M. Pfeffer, J. Organomet. Chem. 104 (1976) 377.

168. M.L.H. Green, T. Luong-thi, G.A. Moser, I.Packer, F. Pettit, and D.M. Roe, J.C.S. Dalton (1976) 1988.

169. M.L.H. Green, R.E. MacKenzie, and J.S. Poland, J.C.S. Dalton (1976) 1993.

170. K. Oefele, E. Roos and M. Herberhold, Z. Naturforsch. 31B (1976) 1070.

171. E.O. Fischer, K. Scherzer, and F.R. Kreissl, J. Organomet. Chem. 118 (1976) C33.

172. H. Brunner, J. Doppelberger, E.O. Fischer, and M. Lappus, J. Organomet. Chem. 112 (1976) 65.

173. C.P. Casey and W.R. Brunsvold, J. Organomet. Chem. 118 (1976) 309.

174. K. Weiss and E.O. Fischer, Chem. Ber. 109 (1976) 1120.

175. E.O. Fischer and K. Weiss, Chem. Ber. 109 (1976) 1128.

176. E.O. Fischer, W. Kleine, and F.R. Kreissl, J. Organomet. Chem. 107 (1976) C23.

177. E.O. Fischer, W. Kleine, and F.R. Kriessl, Angew. Chem. Int. Ed. Engl. 15 (1976) 616.

178. F.R. Kreissl, E.W. Meineke, E.O. Fischer, and J.D. Roberts, J. Organomet. Chem. 108 (1976) C29.

179. T.J. Katz, S.J. Lee, and N. Acton, Tet. Lett. 47 (1976) 4247.

180. T.J. Katz and N. Acton, Tet. Lett. 47 (1976) 4251.

181. E.O. Fischer and K. Richter, Chem. Ber. 109 (1976) 1140.

182. E.O. Fischer and W. Held, J. Organomet. Chem. 112 (1976) C59.

183. E.O. Fischer, H. -J. Kalder, A. Frank, F.H. Kohler, and G. Huttner, Angew. Chem. Int. Ed. Engl. 15 (1976) 623.

184. E.O. Fischer and S. Riedmüller, Chem. Ber. 109 (1976) 3358.

185. K.H. Dötz, R. Dietz, A. von Imhof, H. Lorenz and G. Huttner, Chem. Ber. 109 (1976) 2033.

186. H.G. Raubenheimer and S. Lotz, J.C.S. Chem. Comm. (1976) 732.

187. C.G. Kreiter, K. Öfele and G.W. Weiser, Chem. Ber. 109 (1976) 1749.

188. K.H. Dötz, J. Organomet. Chem. 118 (1976) C13.

189. K.H. Dötz and C.G. Kreiter, Chem. Ber. 109 (1976) 2026.

190. H.G. Raubenheimer, J.C.A. Boeyens, and S. Lotz, J. Organomet. Chem. 112 (1976) 145.

191. K. Weiss and E.O. Fischer, Chem. Ber. 109 (1976) 1868.

192. P. Jutzi and W. Steiner, Angew. Chem. Int. Ed. Engl. 15 (1976) 684.

193. P. Jutzi and W. Steiner, Chem. Ber. 109 (1976) 3473.

194. W.K. Dean and W.A.G. Graham, J. Organomet. Chem. 120 (1976) 73.

195. E.O. Fischer and G. Kreis, Chem. Ber. 109 (1976) 1673.

196. E.O. Fischer and K. Richter, Chem. Ber. 109 (1976) 2547.

197. A.J. Hartshorn and M.F. Lappert, J.C.S. Chem. Comm. (1976) 761.

198. E.O. Fischer, T.L. Lindner, and F.R. Kreissl, J. Organomet. Chem. 112 (1976) C27.

199. E.O. Fischer and K. Richter, Chem. Ber. 109 (1976) 3079.

200. E.O. Fischer, P. Stückler, H. -J. Beck and F.R. Kreissl, Chem. Ber. 109 (1976) 3089.

201. E.O. Fischer, M. Schluge, and J.O. Besenhard, Angew. Chem. Int. Ed. Engl. 15 (1976) 683.

202. E.O. Fischer, G. Huttner, T.L. Lindner, A. Frank, and F.R. Kreissl, Angew. Chem. Int. Ed. Engl. 15 (1976) 157.

203. K. Richter, E.O. Fischer, and C.G. Kreiter, J. Organomet. Chem. 122 (1976) 187.

204. F.R. Kreissl and P. Stueckler, J. Organomet. Chem. 110 (1976) C9.

205. F.R. Kreissl, A. Frank, U. Schubert, T.L. Lindner, and G. Huttner, Angew. Chem. Int. Ed. Engl. 15 (1976) 632.

206. F.R. Kreissl, W. Uedelhoven, and A. Ruhs, J. Organomet. Chem. 113 (1976) C55.

207. E.O. Fischer and W.R. Wagner, J. Organomet. Chem. 116 (1976) C21.

208. I. Fischler, M. Budzwait, and E.A. Koerner von Gustorf, J. Organomet. Chem. 105 (1976) 325.

209. D. Rietvelde and L. Wilputte-Steinert, J. Organomet. Chem. 118 (1976) 191.

210. D.J. Darensbourg and A. Salzer, J. Organomet. Chem. 117 (1976) C90.

211. A. Salzer, J. Organomet. Chem. 117 (1976) 245.

212. M.L.H. Green and John Knight, J.C.S. Dalton (1976) 213.

213. A.T.T. Hsieh and B.O. West, J. Organomet. Chem. 112 (1976) 285.

214. A. Cutler, D. Ehntholt, W.P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, J. Am. Chem. Soc. 98 (1976) 3495.

215. K.H. Pannell, M.F. Lappert, and K. Stanley, J. Organomet. Chem. 111 (1976) 37.

216. J.W. Faller and A.M. Rosan, J. Am. Chem. Soc., 98 (1976) 3388.

217. H.G. Alt, Angew. Chem. Int. Ed. Engl. 15 (1976) 759.

218. R.D. Adams and D.F. Chodosh, J. Am. Chem. Soc. 98 (1976) 5391.

219. A.R. Siedle, J. Organomet. Chem. 120 (1976) 369.

220. H. Alper and G. Wall, J.C.S. Chem. Comm. (1976) 263.

221. J. Sobczak and J.J. Ziolkowski, Inorg. Chim. Acta, 19 (1976) 15.

222. J. Levisalles, H. Rudler, and D. Villemin, J. Organomet. Chem. 122 (1976) C15.

223. K. Iuchi, S. Asada, T. Kinugasa, K. Kanamori and A. Sugimori, Bull. Chem. Soc. Japan 49 (1976) 577.

224. D.T. Laverty, M.A. McKervey, J.J. Rooney, and A. Stewart, J.C.S. Chem. Comm. (1976) 193.

225. R.F. Howe, Inorg. Chem. 15 (1976) 486.

226. C.E. McKenna, M. -C. McKenna, and M.T. Higa, J. Am. Chem. Soc. 98 (1976) 4657.

227. T. Okuhara, K. -I. Tanaka and K. Miyahara, J.C.S. Chem. Comm. (1976) 42.

228. T. Okuhara and K. -I. Tanaka, J.C.S. Chem. Comm. (1976) 199.

229. K. Ichikawa, T. Takagi and K. Fukuzumi, Bull. Chem. Soc. Japan 49 (1976) 750.

230. J.L. Bilhou, J.M. Basset, R. Mutin, and W.F. Graydon, J.C.S. Chem. Comm. (1976) 970.

231. S.J. Lee, J. McGinnis, and T.J. Katz, J. Am. Chem. Soc. 98 (1976) 7818.

232. M.F. Farona and V.W. Motz, J.C.S. Chem. Comm. (1976) 930.

233. M.T. Mocella, R. Rovner, and E.L. Muetterties, J. Am. Chem. Soc. 98 (1976) 4689.

234. R. Taube, K. Seyferth, L. Bencze, and L. Marko', J. Organomet. Chem. 111 (1976) 215.

235. N. Calderon, E.A. Ofstead, and W.A. Judy, Angew. Chem. Int. Ed. Engl. 15 (1976) 401.

236. M. Ephritikhine, M.L.H. Green, and R.E. MacKenzie, J.C.S. Chem. Comm. (1976) 619.

237. M. Ephritikhine and M.L.H. Green, J.C.S. Chem. Comm. (1976) 926.

238. J. McGinnis, T.J. Katz, S. Hurwitz, J. Am. Chem. Soc. 98 (1976) 605.

239. C.P. Casey, H.E. Tuinstra, and M.C. Saeman, J. Am. Chem. Soc. 98 (1976) 608.

240. T.J. Katz, J. McGinnis, and C. Altus, J. Am. Chem. Soc. 98 (1976) 606.

241. M.T. Mocella, M.A. Busch, and E.L. Muetterties, J. Am. Chem. Soc. 98 (1976) 1283.

242. T.J. Katz and R. Rothchild, J. Am. Chem. Soc. 98 (1976) 2519.

243. R.H. Grubbs, D.D. Carr, C. Hoppin, and P.L. Burk, J. Am. Chem. Soc. 98 (1976) 3478.

244. P.G. Gassman and T.H. Johnson, J. Am. Chem. Soc. 98 (1976) 6055.

245. P.G. Gassman and T.H. Johnson, J. Am. Chem. Soc. 98 (1976) 6057.

246. P.G. Gassman and T.H. Johnson, J. Am. Chem. Soc. 98 (1976) 6058.

247. P.G. Gassman and T.H. Johnson, J. Am. Chem. Soc. 98 (1976) 861.

248. J.D. Atwood and T.L. Brown, J. Am. Chem. Soc. 98 (1976) 3160.

249. J.E. Pardue and G.R. Dobson, Inorg. Chim. Acta 20 (1976) 207.

250. M.Y. Darensbourg and N. Walker, J. Organomet. Chem. 117 (1976) C68.

251. M.A. Cohen and T.L. Brown, Inorg. Chem. 15 (1976) 1417.

252. D.J. Darensbourg, G.R. Dobson, and A. Moradi-Araghi, J. Organomet. Chem. 116 (1976) C17.

253. L.D. Schultz and G.R. Dobson, J. Coord. Chem. 5 (1976) 163.

254. J.A. Connor and P.I. Riley, J.C.S. Chem. Comm. (1976) 149.

255. J.A. Connor and P.I. Riley, J.C.S. Chem. Comm. (1976) 634.

256. C.M. Elson, Inorg. Chem. 15 (1976) 469.

257. B. Caro and G. Jaouen, J.C.S. Chem. Comm. (1976) 655.

258. J.R. Chipperfield, J. Ford, A.C. Hayter, and D.E. Webster, J.C.S. Dalton (1976) 360.

259. J.R. Chipperfield, J. Ford, A.C. Hayter, D.J. Lee and D.E. Webster, J.C.S. Dalton (1976) 1024.

260. J.H. Espenson and J.P. Leslie, II, Inorg. Chem. 15 (1976) 1886.

261. M. Basato, J.C.S. Dalton (1976) 1678.

262. J.K. Burdett, R.N. Perutz, M. Poliakoff and J.J. Turner, Inorg. Chem. 15 (1976) 1245.

263. L.H. Jones, Inorg. Chem. 15 (1976) 1244.

264. I.S. Butler, A. Garcia-Rodriguez, K.R. Plowman, and C.F. Shaw, III, Inorg. Chem. 15 (1976) 2602.

265. D. Kariuki and S.F.A. kettle, J. Organomet. Chem. 105 (1976) 209.

266. G. Davidson and D.A. Duce, J. Organomet. Chem. 120 (1976) 229.

267. V.N. Trembovler, N.K. Baranetskaya, N.V. Fok, G.B. Zaslavskaya, B.M. Yavorskii, and V.N. Setkina, J. Organomet. Chem. 117 (1976) 339.

268. A. Nakamura and S. Otsuka, Bull. Chem. Soc. Japan 49 (1976) 3641.

269. F. Van Meurs, J.M. Van der Toorn, and H. Van Bekkum, J. Organomet. Chem. 113 (1976) 341.

270. V. Graves and J.J. Lagowski, J. Organomet. Chem. 120 (1976) 397.

271. G. Hunter and R.C. Massey, J.C.S. Dalton (1976) 2007.

272. D.A. Brown, N.J. Fitzpatrick, I.J. King, and N.J. Mathews, J. Organomet. Chem. 104 (1976) C9.

273. V. Graves and J.J. Lagowski, Inorg. Chem. 15 (1976) 577.

274. K. Eberl, F.H. Kohler, and L. Mayring, Angew. Chem. Int. Ed. Engl. 15 (1976) 554.

275. K.H. Köhler, J. Organomet. Chem. 110 (1976) 235.

276. M.H. Chisholm, F.A. Cotton, M. Extine, M. Millar, and B.R. Stults, Inorg. Chem. 15 (1976) 2244.

277. D.S. Milbrath and J.G. Verkade, Inorg. Nucl. Chem. Lett. 12 (1976) 921.

278. H.C.E. McFarlane, W. McFarlane and D.S. Rycroft, J.C.S. Dalton (1976) 1616.

279. B. Rees and A. Mitschler, J. Am. Chem. Soc. 98 (1976) 7918.

280. R. Hoffmann, J.M. Howell, and A.R. Rossi, J. Am. Chem. Soc. 98 (1976) 2484.

281. R.H. Summerville and R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 7240.

282. K. Tatsumi and T. Fueno, Bull. Chem. Soc. Japan 49 (1976) 929.

283. F. Kinomura, T. Tamura, I. Watanabe, Y. Yokoyama and S. Ikeda, Bull. Chem. Soc. Japan 49 (1976) 3544.

284. D.L. Lichtenberger and R.F. Fenske, Inorg. Chem. 15 (1976) 2015.

285. J.W. Lauber, M. Elian, R.H. Summerville, and R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 3219.

286. T.F. Block, R.F. Fenske, and C.P. Casey, J. Am. Chem. Soc. 98 (1976) 441.

287. R. Hoffmann and P. Hoffmann, J. Am. Chem. Soc. 98 (1976) 598.

288. C. Azokpota, C. Pommier, Y. Limouzin, and J.C. Maire, J. Organomet. Chem. 117 (1976) 349.

289. D.W. Clack, M. Monshi, and L.A.P. Kane-Maguire, J. Organomet. Chem. 120 (1976) C25.

290. J.W. Lauber and R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.

291. D.R. Armstrong, R. Fortune, and P.G. Perkins, J. Organomet. Chem. 111 (1976) 197.

292. R.H.T. Bleijerveld and K. Vrieze, Inorg. Chim. Acta 19 (1976) 195.

293. P. Paoletti, L. Fabbrizzi, and R. Mascherini, J. Chem. Soc. 72 (1976) 896.

294. G.A. Domrachev and V.D. Zinovev, J. Organomet. Chem. 117 (1976) 241.

295. F.A. Adedeji, J.A. Connor, and H.A. Skinner, J.C.S. Chem. Comm. (1976) 159.

296. C.J. Pickett and D. Pletcher, J.C.S. Dalton (1976) 749.

297. R.D. Rieke, H. Kojima and K. Oefele, J. Am. Chem. Soc. 98 (1976) 6735.

298. A.M. Bond and R. Colton, Inorg. Chem. 15 (1976) 446.

299. M.A.M. Meister, R.C.J. Vriends, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta 19 (1976) 95.

300. P.J. Krusic, U. Klabunde, C.P. Casey and T.F. Block, J. Am. Chem. Soc. 98 (1976) 2015.

301. K.R. Gordon and K.D. Warren, J. Organomet. Chem. 117 (1976) C27.

302. Y.S. Nekrasov and N.I. Vasyukova, J. Organomet. Chem. 122 (1976) 227.

303. I.G. deJong and D.R. Wiles, Inorg. Chem. 15 (1976) 2588.

304. P.E. Riley and R.E. Davis, Inorg. Chem. 15 (1976) 2735.

305. M.H. Chisholm, M. Extine, and W. Reichert, Proc. Int. Conf. Coord. Chem., 16th, 1974.

306. P.E. Riley and R.E. Davis, Inorg. Chem. 15 (1976) 2735.

307. C.T. Lam, D.L. Lewis, and S.J. Lippard, Inorg. Chem. 15 (1976) 989.

308. T. Debaerdemacker, Angew. Chem. Int. Ed. Engl. 15 (1976) 504.

309. A.M. Ciplys, R.J. Geue, and M.R. Snow, J.C.S Dalton (1976) 35.

310. M.H. Chisholm, F.A. Cotton, M. Extine and B.R. Stults, Inorg. Chem. 15 (1976) 2252.

311. N.G. Connelly, B.A. Kelly, R.L. Kelly and P. Woodward, J.C.S. Dalton (1976) 699.

312. Y.T. Struchkov, V.G. Andrianov, A.N. Nesmeyanov, V.V. Krivykh, V.S. Kaganovich and M.I. Rybinskaya, J. Organomet. Chem. 117 (1976) C81.

313. J.A.K. Howard, R.F.D. Stansfield, and P. Woodward, J.C.S. Dalton (1976) 246.

314. G. Schmidt and R. Boese, Chem. Ber. 109 (1976) 2148.