SUBSTITUTION PRODUCTS OF THE GROUP VIB METAL CARBONYLS

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I. Introduction†

The recent rapid expansion of the chemistry of the metal carbonyls has rendered difficult a comprehensive review of the field and, since many past reviews have treated derivatives of the metal carbonyls within broader classes of compounds, e.g., aryl, cyclopentadienyl, or olefinic transition

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† Key to abbreviations used:

aca—acetylacetonate	D—donor
Ar—arene	diars—*o*-phenylenebis(dimethylarsine)
Bu—butyl	dien—diethylenetriamine
Cp—cyclopentadienyl	diglyme—bis(2-methoxyethyl) ether

metal complexes, it was thought a review of the carbonyl derivatives of a single metallic subgroup, VIB (Cr, Mo, W), might prove to be of interest. This subgroup was chosen because of the authors' particular interest in it and because the derivatives of the octahedral metal carbonyls should prove to be of the widest general interest.

Several review articles in recent years have touched upon the subject of this review. Wherever practical, duplication of material will be avoided and the reader will be referred to one of the several reviews for earlier work in the field. Metal-carbon bonding has been reviewed by Richardson (*259*); the arene and cyclopentadienyl metal carbonyls have been discussed by Wilkinson and Cotton (*330*), Fischer and Fritz (*108, 109*), Pauson (*246*), and Zeiss (*337*); olefinic derivatives by Guy and Shaw (*151*), Fischer and Werner (*139, 140*), and Bennett (*39*); anionic carbonyl derivatives by Hieber *et al.* (*160*) and King (*185b*); derivatives of phosphines, arsines, and stibines by Booth (*48*); ultraviolet-induced reactions of the metal carbonyls by Strohmeier (*284*); and the metal carbonyls in general have recently been reviewed by Chatt *et al.* (*64*), Abel (*1*), and Malatesta (*211*).

It will be noted that few of the reviews cited deal with coordinately bonded derivatives: it is to this subject that the present review will be largely addressed.

An attempt has been made to review the literature to January, 1965; in some instances later material has been incorporated. References are believed complete to September, 1965.

II. Derivatives of Coordinately Bonded Ligands

A. Bonding

1. *Introduction*

In the years following World War II, the increasingly large body of experimental data inconsistent with widely held beliefs led to a reassess-

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dipy—2,2′-dipyridyl
DMF—dimethylformamide
DMSO—dimethylsulfoxide
DTH—2,5-dithiahexane
en—ethylenediamine
Et—ethyl
i—iso-
Me—methyl
MF—methylformamide
phen—1,10-phenanthroline
ϕ—phenyl
pip—piperidine
Pr—propyl
py—pyridine
quin—quinoline
TDP—tris(dimethylamino)phosphine
tere—terephthalic acid dimethyl ester
THF—tetrahydrofuran
triars—methylbis(3-propyldimethylarsine)arsine
trien—triethylenetetramine
tripy—2,2′,2″-tripyridyl
TTU—3,6,9-trithiaundecane

ment of the mechanism of bonding in certain transition metal complexes. Among the anomalous observations (*85*) were:

(a) The inability in many instances of workers to relate the stability of transition metal complexes to the charge-donating characteristics of the ligand.

(b) Anomalously short bond lengths in certain transition metal complexes, e.g., the metal carbonyls.

(c) The ability of certain weakly basic ligands, e.g., CO and PF_3, unable to form complexes with elements such as B, Al, and Ga, to form strong bonds with transition metals.

(d) The nonpolar nature of metal-ligand bonds, as in the PF_3 complexes of Pt, inexplicable in terms of coordinate bonding alone.

Common characteristics in complexes exhibiting anomalous behavior were the availability of filled metallic *d* orbitals and of vacant ligand orbitals with which they could interact.

2. Bonding in Metal Carbonyls

The now accepted bonding mechanism may be exemplified by consideration of bonding in the octahedral metal carbonyls, e.g., $Cr(CO)_6$. Bonding involves both coordinate σ-bond formation, in which the lone pairs of electrons on the carbon atoms interact with vacant metallic orbitals (Fig. 1), and metal-ligand π-bonding, in which filled metallic *d* orbitals interact with low-lying vacant antibonding π orbitals of the CO groups (Fig. 2). A molecular orbital energy-level diagram for an octahedral metal carbonyl is given in Fig. 3 (*149*). The two modes of bonding are mutually reinforcing, "synergic"; charge removal from the metal through π "back bonding" leads to more extensive σ-bond formation, while the charge thus donated to the metal facilitates further back bonding. The Group VIB

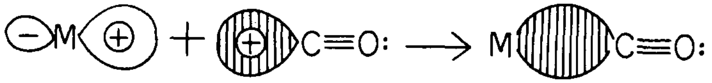


FIG. 1. CO → M σ-bond formation.

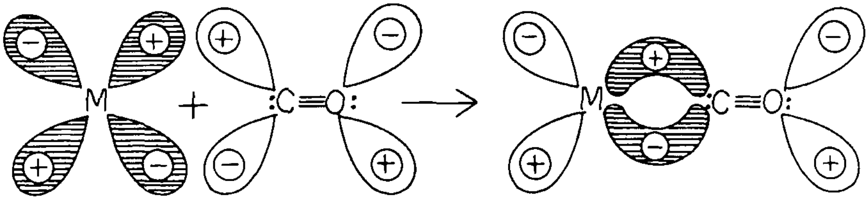


FIG. 2. M → CO $d\pi - p\pi^*$ "back bonding."

metal carbonyls, and their simple substitution products with various coordinating ligands, obey Sidgwick's rule, have the electronic configuration of the next rare gas, and thus are diamagnetic.

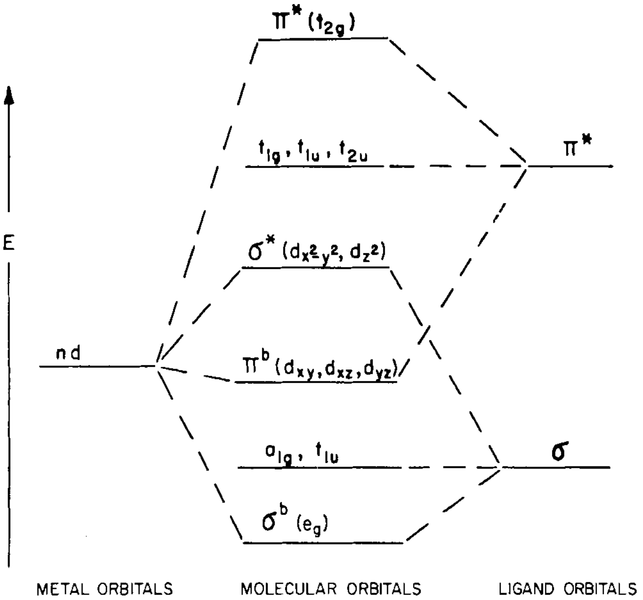


FIG. 3. Schematic molecular orbital energy-level diagram for $M(CO)_6$. Only *nd* metal and σ and π^* ligand interactions shown. Level spacings qualitative [adapted from Gray and Beach (*149*)].

3. Types of Coordinate Bonding in Substitution Products

Coordinate bonding in mixed metal carbonyl complexes may be classified as involving (a) d_π—p_π back bonding, (b) d_π—d_π back bonding, or (c) no back bonding.

(a) Ligands which accept charge through d_π—p_π back bonding (Fig. 2) have, in addition to a lone pair of electrons, either multiply bonded atoms possessing low-lying p_π^* orbitals, e.g., CO and CN^-, or are heterocyclic aromatic ring systems, such as py or phen, in which back bonding takes place through interaction of filled metallic *d* orbitals with the appropriate molecular orbitals of the p_π aromatic system.

(b) For ligands which accept charge through d_π—d_π back bonding, the coordinating atom possesses vacant *d* orbitals (Fig. 4). The extent of back bonding varies widely for these ligands and appears to be, to a marked degree, a function of the electronegativities of substituents on the donor atom.

(c) Ligands such as amines, amides, ketones, and alcohols are struc-

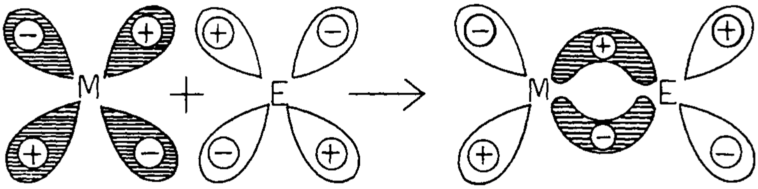


FIG. 4. M → D $d\pi - d\pi$ "back bonding."

turally unable to accept metallic charge, but their mixed carbonyl complexes are stabilized to a degree by the ability of the undisplaced carbonyl groups to accept a part of the charge they donate to the metal.

Studies of carbon-oxygen bonding in mixed metal carbonyl complexes have been used to determine the effects of changes in the net charge on the metal which result from the displacement of CO groups (Section B). The extent of CO π-acceptance of metallic charge in the carbonyls may be qualitatively gauged through comparison of CO stretching frequencies of CO and the metal carbonyls. Thus, ν_{CO} for free CO is 2133 cm^{-1} (*152*), while the infrared-active T_{1u} mode for the gaseous hexacarbonyls is approximately 2000 cm^{-1} (*49*), indicating extensive occupancy of the CO π^* orbitals by metallic electrons in the complex. The effect of increased negative charge on the metal atom is apparent in changes of ν_{CO} for the isoelectronic series $Mn(CO)_6^+$, $Cr(CO)_6$, and $V(CO)_6^-$. The respective CO stretching frequencies are 2096, 2000, and 1859 cm^{-1} (*165*), again reflecting the increasing mixing of π and π^* orbitals of CO, which corresponds to a greater contribution of structure (1b) to a resonance description of the M—C—O bonding:

$$\underset{(1a)}{M{-}C{\equiv}O} \leftrightarrow \underset{(1b)}{M^+{=}C{=}O^-} \qquad (1)$$

Two recent estimates of the π-accepting ability of CO in $M(CO)_6$ place it at ~0.1–0.2 electron pairs per CO (*93a, 148a*).

Most substituent groups have a net charge-donating effect in competition with CO and thus produce decreases in CO stretching frequencies and bond orders, with corresponding increases in M—C stretching and M—C—O deformation frequencies. For "typical" ligands, therefore, displacement of CO becomes increasingly difficult with more extensive substitution, and decreases in CO stretching frequencies with increased displacement are also noted. Complete displacement of CO from the hexacarbonyls has been achieved only for polydentate ligands (*24*, *28*) and with PF_3 (*173*, *198*, *199*, *200*). The latter is an "atypical" ligand, in that it is quite similar to CO in π-accepting ability (*173*). Conversely, for TDP only disubstitution has been effected (*183*); it is postulated that partial delocalization of the lone pair on nitrogen into the vacant 3*d* orbitals of P renders them less effective as π-acceptors, although it also seems possible that steric hindrance might prevent the bulky TDP groups from entering equatorial positions in the molecule.

The strengthening of M—C bonds with the increased net charge-donating properties of coordinating groups is reflected in the data of Poilblanc and Bigorgne (*254*), who have measured the relative rates of CO displacement by PEt_3 and PCl_3 from $Mo(CO)_6$ at different temperatures (Fig. 5). The curves indicate a greater ease of displacement by PCl_3, which introduces a lesser amount of charge on the metal, as is indicated by the respective CO stretching force constants for their derivatives (Table II).

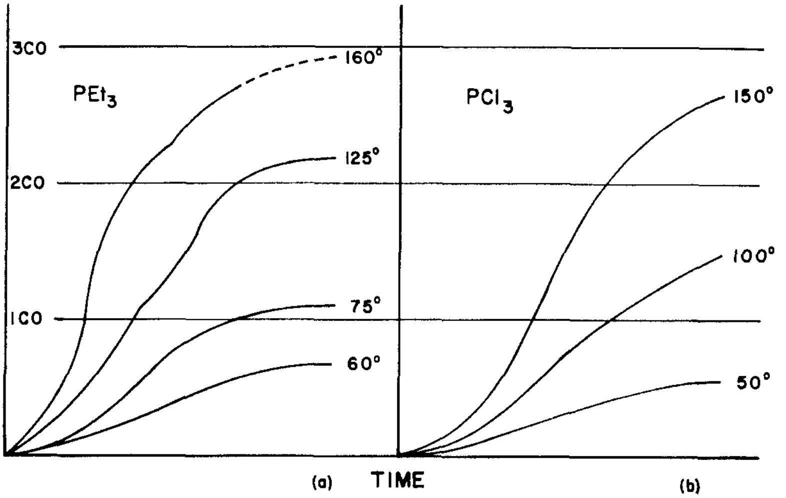


FIG. 5. Relative rates of displacement of CO from $Mo(CO)_6$ by (a) Et_3P; (b) PCl_3 [from Poilblanc and Bigorgne (*254*)].

Studies by Nyholm and co-workers (*18*) have shown that the extent of ν_{CO} solvent shifts in more polar solvents increases with more extensive displacement of CO groups, and with the concomitant decreases in ν_{CO}. These results point to increased dipole-dipole interactions between CO groups and solvent molecules as the negative charge on the metal is augmented, and indicate, therefore, a greater contribution of structure (b) in Eq. (1) to the resonance description of the bonding.

4. Donor-Acceptor Properties of Coordinating Groups

Studies of the relative decreases of CO and NC stretching frequencies in $ArCr(CO)_2$ (isonitrile) complexes, in which the arene groups have varying charge-donating abilities, indicate that the isonitrile group is able to compete on favorable terms with CO for metallic *d* electrons (*297*). Partial bond moments for these complexes (Table I) also suggest appreciable π-accepting ability on the part of isonitrile ligands, as do the relatively high

CO stretching frequencies for their derivatives (Table II). Other infrared studies, however, support a more limited π-accepting ability for isonitriles (*45, 82*). Heterocyclic ring systems, e.g., py, dipy, and phen, in which coordination is through the hetero atom but which nonetheless accept charge through the aromatic p_π system, appear to be relatively poor acceptors. Specific examples of bonding by such ligands are discussed in Section D,1.

There is some question as to what interpretation may be made of changes in CO stretching frequencies in mixed derivatives with respect to the relative σ- and π-bonding abilities of various ligands. In the hexacarbonyls, on the basis of O_h symmetry, metallic valence orbitals cannot simultaneously be used for both σ- and π-bonding, and thus σ- and π-bonding in such systems may be treated independently ("symmetry factoring") (*77*). This is not, however, the case for their substitution products (*181b*). Present experimental evidence nonetheless indicates, in general, that it is a reasonable approximation that σ- and π-bonding in derivatives of the Group VIB metal carbonyls may be "symmetry factored." Thus Cotton (*76*) has proposed that changes in CO stretching frequencies with different donor groups are a function only of the π-accepting ability of the ligand in question, and that all $M(CO)_5D$ complexes in which there is no M—D π-bonding should have roughly similar CO stretching frequencies and force constants. In the opinion of Bigorgne and co-workers, however, changes in ν_{CO} with different substituents on P, As, and Sb for analogous mixed carbonyl complexes are primarily an inductive phenomenon, affecting the σ-donating ability of the Group VA atom (*43, 50, 254*).

Many groups coordinating through N or O, e.g., amines, alcohols, and ethers, possess no low-lying vacant orbitals through which metallic charge can be accepted. Evidence indicates that N is a superior donor to O. This conclusion may be inferred from the stabilities of analogous O- and N-bonded addition complexes of BF_3 (*277*), and from the generally greater stability exhibited by the mixed metal carbonyl complexes of N-bonded ligands relative to those bonded through O. The available data show that ν_{CO} frequencies for $M(CO)_5D$ complexes bonded through O or N are similar (Table II), lending support to the view of Cotton and Kraihanzel. However, as Abel (*1*) has pointed out, ν_{CO} frequencies for $Mo(CO)_3$(diglyme) are considerably higher than those for the analogous $Mo(CO)_3$(dien) (Table II), and this observation might be interpreted in terms of the greater electronegativity, and thus poorer donating ability, of O.

P, As, Sb, and Bi in Group VA, and S, Se, and Te in Group VIA, have vacant d orbitals available for d_π—d_π back bonding. The relative σ-donating abilities of ligands bonding through these atoms may again be estimated from the stabilities of their addition complexes, e.g., with $AlCl_3$ (*277*). The orders of donating ability are P > As > Sb > Bi, and S > Se > Te.

Similar studies show that ligands bonding through Group VA atoms generally are superior donors to the analogous Group VIA ligands. As has been indicated, the relative π-bonding abilities of ligands are difficult to infer on the basis of the CO stretching frequencies in their mixed complexes. This is particularly true for the mixed complexes of Group VA ligands, for which CO stretching frequencies remain essentially constant for analogous derivatives (Table II). This would be consistent with an essentially constant, or slightly decreasing, π-accepting ability down the group. Two countervening factors to consider in this regard are the increasing diffuseness of ligand *d* orbitals with increasing atomic number, which results in poorer d_π—d_π overlap, and the greater stability of these orbitals at higher *Z*.

Strohmeier and co-workers (*204*, *297*, *298*) have derived equations which may be used to calculate the partial bond moments for M—D bonds in derivatives of the type $ArM(CO)_2D$. Since M—D bond strength should vary as the sum of the σ-donating and π-accepting abilities of a ligand, a comparison of the stabilities of various $ArM(CO)_2D$ complexes with the partial bond moments of their M—D bonds can lead to estimates of the relative σ-donating and π-accepting strengths of various D. Table I gives the partial bond moments for M—D bonds, the relative stabilities of $(tere)Cr(CO)_2D$ complexes, and the inferred relative σ-donor and π-acceptor strengths of the groups D (*295*, *298*). For example, the most stable complex, $(tere)Cr(CO)_2(CO)$, has the smallest partial bond moment, and it may be inferred that σ-donating and π-accepting abilities of CO differ rather little, but that their sum is large.

TABLE I

Relative σ-Donating and π-Accepting Strengths for Ligands D in $(tere)Cr(CO)_2D$ Complexes (*298*)

Ligand	pip	quin	$P\phi_3$	$\phi CN\rightarrow$	$C_6H_{11}NH\rightarrow$	CO
μ(D—M) (debyes)	4.0	3.9	3.1	2.1	2.0	0.8
Order of complex stability (1 = most stable)	5	3	2	5	4	1
Inferred relative bond strengths						
σ-Donor	Large	Large	Large	Medium	Medium	Large
π-Acceptor	None	Small	Medium	Small	Medium	Large

5. *Bonding and Stereochemistry*

The directional nature of metallic *d* orbitals allows an oversimplified but useful explanation of the directive influence of one substituent group upon the next. The π-bonding interpretation of the *trans* effect for planar complexes, that a π-accepting ligand labilizes the *trans* position by withdrawing charge from it and thus facilitating nucleophilic attack by an incoming ligand (*243*), may be modified to apply to the present case. Here, since the carbonyl groups are usually the superior π-acceptors in mixed carbonyl complexes, the position *trans* to the substituent should be the least likely position for attack. Failure of a ligand to remove effectively the charge it donates to the metal results in the redistribution of a greater portion of it to the *trans* position than to the other four, equivalent positions. This results in a greater contribution of $M^{+}{=}C{=}O^{-}$ at the *trans* position. The effect is simultaneously to strengthen the M—C bond and to place additional charge on the ligand; the latter increases the electrostatic repulsion between the *trans* position and a prospective incoming ligand. The disubstituted derivatives of non-π-accepting ligands, for example those which bond through N or O, are thus invariably the *cis* isomers, while the disubstitution products of phosphines, for example, in which ligand d_π orbitals are available, are either *trans* or *cis*. Steric effects of bulky phosphine ligands also probably inhibit *cis* isomer formation.

B. MOLECULAR SPECTROSCOPY

1. *Infrared Spectra*

a. Carbon-Oxygen Stretching Modes. Band assignments: The numbers and symmetries of infrared- and Raman-active CO stretching fundamentals for the possible geometrical isomers (Fig. 6) of the octahedral derivatives $M(CO)_{6-x}D_x$ may be derived on the basis of the local symmetry of the carbonyl groups undisplaced from the original octahedral array by substituent groups. Structural information about polynuclear complexes can usually be obtained through the assumption that coupling between parts of such molecules may be neglected. For this case the selection rules based upon local symmetry may also be applied. Band assignments have been made on the basis of relative band positions and intensities (*98*, *244*), through complementary Raman data (*254*), and through application of the "nonrigorous" secular equations of Cotton and Kraihanzel (*76*, *77*).

Correct band assignments are a prerequisite to the determination of CO stretching force constants. Orgel (*244*) assumed that the separations between the carbonyl stretching modes in the hexacarbonyls would be of the same approximate magnitude as separations of modes related to these in the substitution products. Bigorgne and co-workers have demonstrated the validity of this rough approximation for a number of phosphine, arsine, and stibine derivatives (*38*, *50*, *254*). On this basis, for example, a separation of approximately 120 cm^{-1} would be expected between the higher A_1

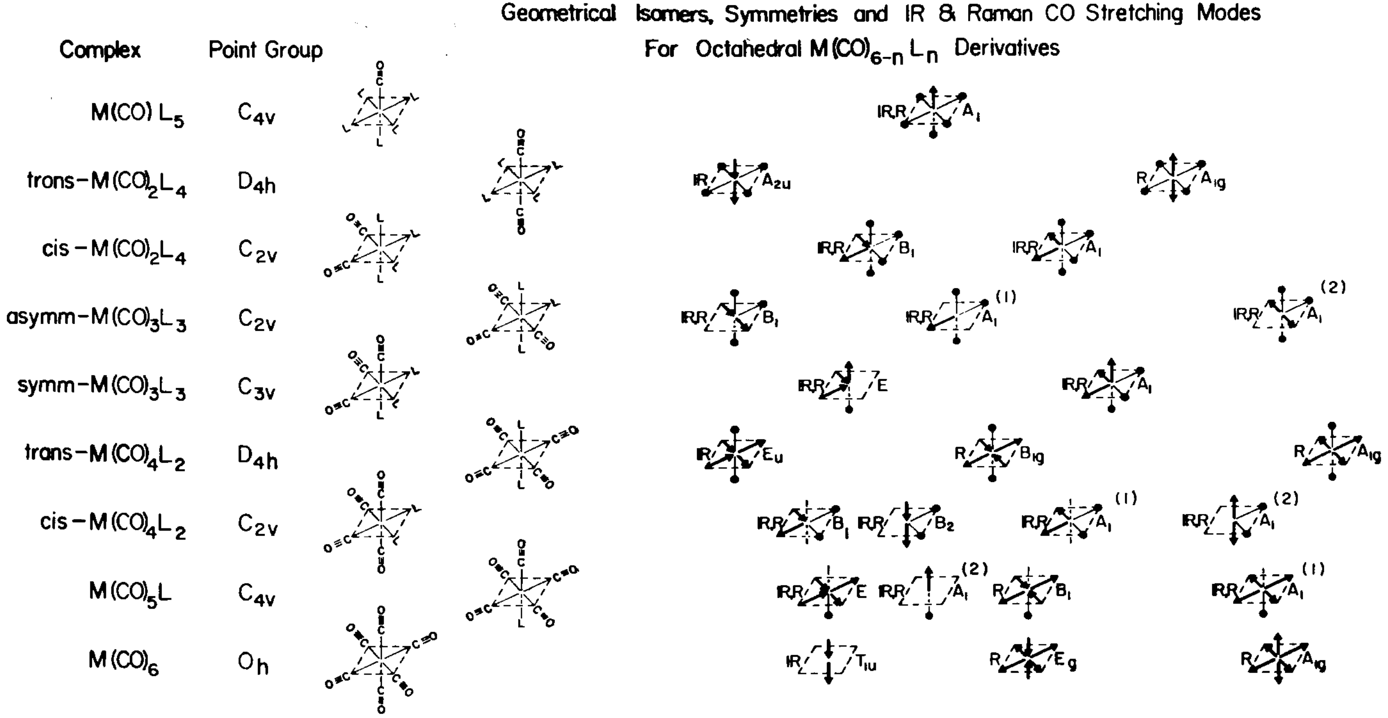


Fig. 6. Geometrical isomers, their symmetries, and infra-red- and Raman-active CO stretching modes for $M(CO)_{6-x}D_x$ derivatives [adapted from Poilblanc and Bigorgne (*254*)].

and the E bands in an $M(CO)_5D$ derivative on the basis of the separation between the A_{1g} and T_{1u} bands for the hexacarbonyls (Table II).

Rough estimates of band intensities have been employed as an assignment aid. Thus, on the basis of an oscillating dipole model, the formally infrared-active $A_1{}^1$ mode (*197*) in $M(CO)_5D$ derivatives, which corresponds to the high-frequency Raman-active A_{1g} "breathing" mode in the hexacarbonyl, would be expected to have a transition moment of zero for four coplanar carbonyl groups perpendicular to the C_4 molecular axis (*98*). Although this condition does not obtain for Group VIB derivatives, because the carbonyls and metal are undoubtedly not coplanar, the mode may nonetheless be assigned as the weakest, highest energy fundamental. This conclusion can also be drawn from the appropriate secular equation under the assumption that all CO—CO stretch-stretch interaction constants for carbonyl substitution products must be positive (see below) (*77*).

The admittedly crude but nonetheless adequate approximations that

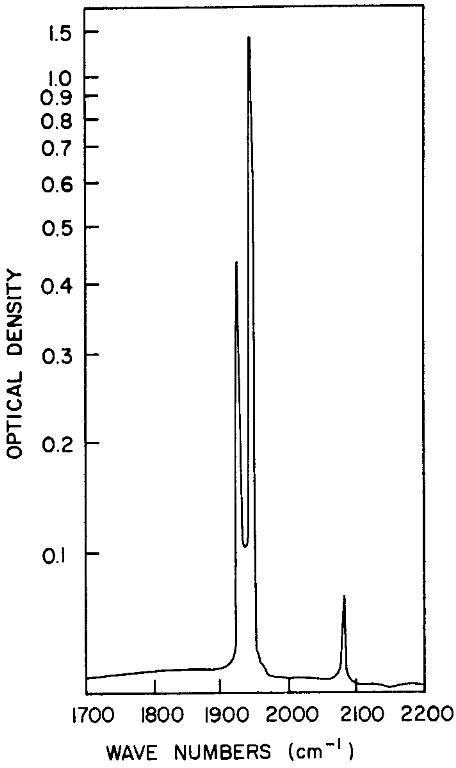


FIG. 7. The infrared spectrum (2200–1700 cm^{-1}) of $W(CO)_5(NCCH_3)$ [from Dobson *et al.* (*95*)].

transition moments in carbonyl groups are constant, and that interaction between carbonyl groups is small, lead to the expectation that for the mono derivative, the E mode, involving the stretching of the four equatorial carbonyls, will have an intensity 4 times that of the *trans* carbonyl A_1^2 mode (*244*). A ratio of about 2.7:1 is observed experimentally for certain complexes (*98*). For the mono derivative, therefore, the three infrared-active CO stretching fundamentals are predicted to be a weak high-frequency band (A_1^1) separated from a strong band (E) by about 120 cm^{-1}, and a third band of intermediate intensity and uncertain position. The validity of these predictions may be judged from a typical spectrum, that of $W(CO)_5(NCCH_3)$ (Fig. 7).

Where an unambiguous assignment cannot be obtained by methods such as these, correct assignments may sometimes be made on their ability to give reasonable force constants when substituted into the appropriate secular equations (*76*, *77*, *197*) (see below).

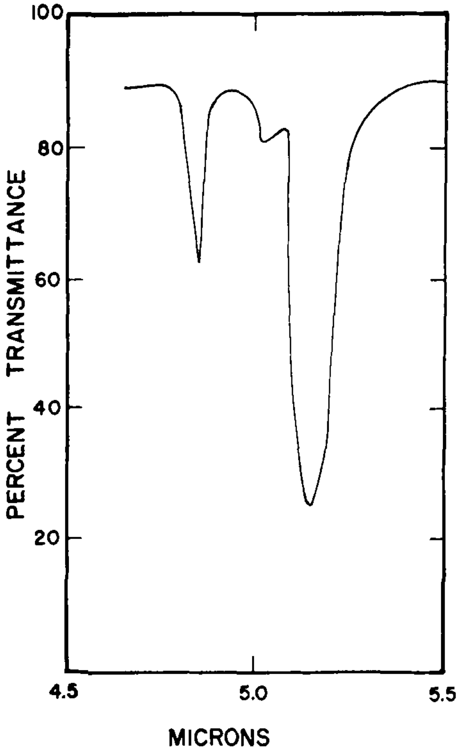


FIG. 8. The infrared spectrum (4.5–5.5 μ) of $Mo(CO)_5(P\phi_3)$. The weak transition ca. 5 μ is infrared-inactive under the approximation of local symmetry [from Cotton and Kraihanzel (*77*)].

Deviations from local symmetry: In many derivatives, transitions formally forbidden under the local symmetry approximation have been observed (*77, 254*). Thus, in many $M(CO)_5D$ phosphine derivatives, the weak band ca. 2000 cm^{-1} has been assigned as the formally infrared-inactive B_1 mode (Fig. 8) (*77*). In this case the C_3 symmetry of the phosphine group reduces the overall molecular symmetry so that all CO stretching modes are infrared-active and nondegenerate. Failure also to observe the expected splitting of the E mode has been attributed to a slight mechanical coupling of CO stretching motions to modes in the phosphine group which could permit the B_1 mode to gain a little additional intensity, without producing detectable splitting in the E mode at the same time (*77*). Similar effects have been noted for the formally forbidden *trans* $M(CO)_4D_2$ modes in complexes containing bulky ligands, e.g., phosphines and cyclic amines (Fig. 9) (*77*).

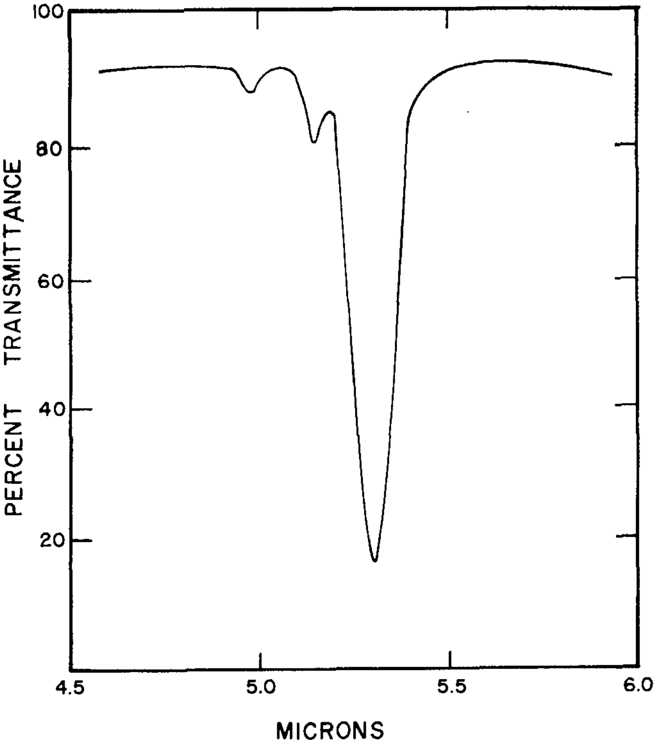


FIG. 9. The infrared spectrum (4.5–6 μ) of *trans*-$Mo(CO)_4(P\phi_3)_2$ [from Cotton and Kraihanzel (*95*)].

Force constants: Cotton and Kraihanzel have derived "nonrigorous" secular equations through which sets of force constants for the series of metal carbonyl derivatives may be obtained (*76, 77*). The equations were derived on the basis of two simplifying assumptions:

(1) No account was taken of coupling between the CO stretching modes and other vibrations of the molecule. This is reasonable in that the CO stretching frequencies are at least 3 times the frequencies of any other molecular vibrations, the highest of which are the M—C—O deformations which occur ca. 600 cm^{-1}. Coupling should, therefore, be slight and, further, that which does occur should not vary appreciably among complexes of a homologous series.

(2) No anharmonicity corrections were made on the observed CO stretching frequencies, nor was an attempt made to correct them for solvent shifts, which often are appreciable, where the frequencies were obtained in different solvents.

Although absolute values for these force constants have no significance and thus cannot be compared to force constants for molecules of different structural type, they are claimed to give internally consistent results for the series of derivatives $M(CO)_{6-x}D_x$.

Useful deductions can be made as to the nature of the force constants:

(1) All CO—CO stretch-stretch interaction force constants should be positive, since π-bonding within a CO group being stretched is weakened, and the π^* orbitals are thus lowered in energy relative to the π^* orbitals of other CO groups. The "nonstretched" CO groups are thus less able to compete for metallic d_π electrons, the "nonstretched" CO bond orders are raised, and the bonds are thus more difficult to stretch.

(2) As a corollary to (1) it is expected that the stretch-stretch interaction force constants will increase with the increased displacement of CO by poorer π-acceptors, since such substitution will increase the number of d_π electrons per CO and magnify the interaction effect.

(3) Interaction constants for pairs of *trans* carbonyls should be approximately twice those for *cis* carbonyls, since *cis* pairs directly share one d_π orbital while *trans* pairs share two.

(4) CO stretching force constants should decrease with increased displacement of CO groups for ligands which are net charge donors.

(5) Force constants for CO groups *cis* to substituents should be greater than those for CO groups *trans* to substituents for ligands which are net charge donors.

CO stretching frequencies and force constants for representative complexes are given in Table II. Trends among the force constants are seen to be consistent with the conclusions as to their nature as stated in the preceding paragraphs.

Cotton has employed the essentially linear relationship between bond orders and CO stretching force constants for simple molecules (Fig. 10) in an effort to determine bond orders for metal carbonyl CO groups (*76*).

It is assumed in this treatment that variations of force constant with bond order for the simple molecules selected correspond to changes in force constant with bond order for the carbonyl derivatives. It is also implicit that changes in carbonyl force constants reflect only differences in metal-ligand π-bonding (Section A,4). The slope of the force constant–bond order relationship (~6.8 md/Å), when applied to (dien)Mo(CO)₃ and (acetonitrile)₃Mo(CO)₃, for example, for which there is a difference of 0.37 md/Å in the force constants (Table II), gives a difference in bond order of 0.37/6.8 or 0.05. This corresponds to a contribution of 0.05 from structure (2b) to a resonance description of the metal-nitrile bonding:

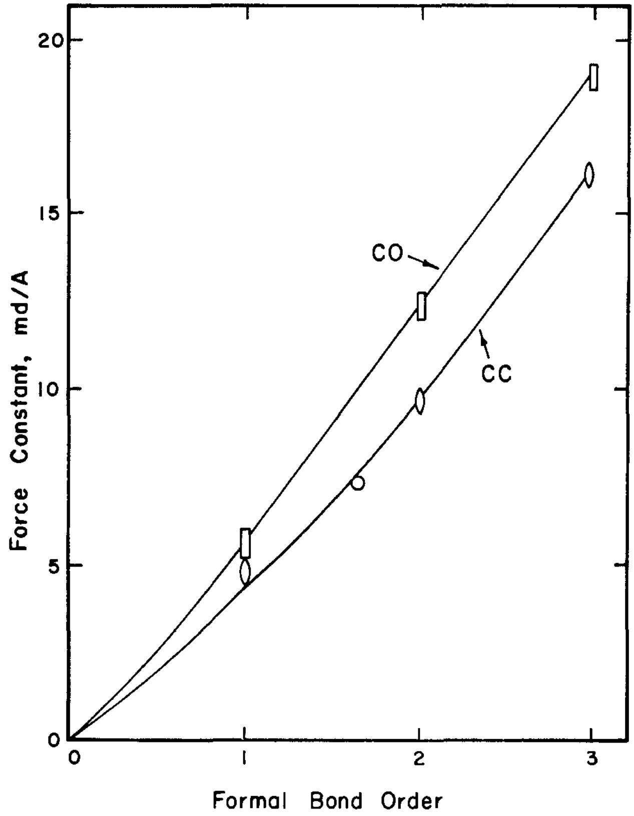


Fig. 10. The relationship between CO and CC stretching force constants and bond rders for simple molecules [from Cotton (76)].

$$\mathrm{R{-}C{\equiv}\overset{+}{N}{-}\overset{-}{M}} \leftrightarrow \mathrm{R{-}\overset{-}{C}{=}\overset{+}{N}{=}M} \qquad (2)$$

(2a) (2b)

TABLE II

SOME REPRESENTATIVE CO STRETCHING FREQUENCIES AND FORCE CONSTANTS FOR $M(CO)_{6-x}D_x$ DERIVATIVES

	cm^{-1}				F_{CO} (*76, 77*) md/Å		
Compound	A_{1g}(R)	E_g(R)	T_{1u}(IR)	Medium^a	k_2	k_i	Ref.
$M(CO)_6$ [O_h]							
$Cr(CO)_6$	~2113	2020.5	2000.1	Gas, hyd.	16.49	0.22	(*49, 88a, 243*)
$Mo(CO)_6$	2119.1	2020.7	2002.6	Gas	16.52	0.27	(*49, 88a*)
$W(CO)_6$	2121.3	2015.2	1997.6	Gas	16.41	0.29	(*49, 88a*)

	cm^{-1}					F_{CO} (*76, 77*) md/Å			
Compound	$A_1^{(2)}$(IR)	B_1(R)	E(IR)	$A_1^{(1)}$(IR)	Medium^a	k_1	k_2	k_i	Ref.
$M(CO)_5D$ [C_{4v}]									
$Mo(CO)_5PF_3$	2104	—	1990	2012	Hyd.	16.57	16.53	0.27	(*173*)
$Mo(CO)_5PCl_3$	2095	—	1985	1999	Hyd.	16.38	16.46	0.26	(*254*)
$Mo(CO)_5P\phi_3$	2073	1984	1952	~1952	Hyd.	15.57	15.99	0.31	(*254*)
$Mo(CO)_5As\phi_3$	2074	—	~1951	~1951	Hyd.	15.56	15.95	0.30	(*60*)
$Mo(CO)_5Sb\phi_3$	2073	—	~1954	~1954	Hyd.	15.58	16.00	0.29	(*38*)
$Mo(CO)_5Bi\phi_3$	2076	—	1957	1946	Hyd.	15.45	16.05	0.29	(*38*)
$Mo(CO)_5S\phi_2$	2081	—	1945	1925	Hyd.	15.12	15.84	0.29	(*174*)
$Mo(CO)_5Se\phi_2$	2077	—	1943	1927	Hyd.	15.20	15.89	0.33	(*174*)
$Mo(CO)_5(NCCH_3)$	2082	—	1953	1925	Hyd.	15.11	16.03	0.32	(*174*)
$Mo(CO)_5(Pr_2O)$	2079	—	1940	1893	Ether	14.65	15.90	0.35	(*275*)
$Mo(CO)_5py$	2079	1987	1944	1890	$CHCl_3$	14.56	15.94	0.34	(*197*)
$Mo(CO)_5(C_6H_{11}NH_2)$	2072	1983	1938	1895	$CHCl_3$	14.65	15.83	0.32	(*197*)
$Mo(CO)_5(MF)$	2072	—	1932	1862	MF	14.15	15.77	0.35	(*275*)
$Mo(CO)_5(DMF)$	2068	—	1924	1847	DMF	13.93	15.67	0.36	(*275*)

TABLE II (*Continued*)

Compound	cm^{-1}			Medium	F_{CO} (*76, 77*) md/Å		Ref.
	A_{1g}(R)	B_{1g}(R)	E_u(IR)		k_2	k_i	
Mo(CO)$_4$(PF$_3$)$_2$	—	—	1988	Hyd.	—	—	(*173*)
Mo(CO)$_4$(PCl$_3$)$_2$	—	—	1984	Hyd.	16.45	0.28^b	(*254*)
Mo(CO)$_4$(Pϕ_3)$_2$	—	1952(?)	1903	Hyd.	15.30	0.34^b	(*254*)
Mo(CO)$_4$(PEt$_3$)$_2$	2018	1937	1887	Hyd.	15.15	0.34	(*254*)

Compound	cm^{-1}				Medium	F_{CO} (*76, 77*) md/Å			Ref.
	$A_1^{(2)}$	B_2	$A_1^{(1)}$	B_1		k_1	k_2	k_i	
M(CO)$_4$D$_2$ [C_{2v}]									
Mo(CO)$_4$(PF$_3$)$_2$	2087	1990	2014	2011	Hyd.	16.59	16.53	0.27	(*173*)
Mo(CO)$_4$(PCl$_3$)$_2$	2072	1992	2002	1984	Hyd.	16.30	16.44	0.27	(*254*)
Mo(CO)$_4$(Pϕ_3)$_2$	2022	1911	1929	1899	Hyd.	14.64	15.41	0.35	(*254*)
Mo(CO)$_4$(DTH)	2030	1905	1919	1868	CHCl$_3$	14.75	15.49	0.37	(*213*)
Mo(CO)$_4$(NCCH$_3$)	2023	1912	1881	1833	Mull	14.08	15.40	0.41	(*260*)
Mo(CO)$_4$(py)$_2$	2025	1907	1881	1839	CHCl$_3$	14.07	15.52	0.42	(*197*)
Mo(CO)$_4$(en)	2015	1890	1864	1818	CH$_3$NO$_2$	13.76	15.25	0.42	(*197*)
W(CO)$_4$(DMF)$_2$	1997	1858	1832	1791	DMF	13.40	14.84	0.45	(*275*)

TABLE II *(Continued)*

Compound	cm^{-1}			Medium	F_{CO} *(76, 77)* md/Å			Ref.
	A_1^2	B_1	A_1^1		k_1	k_2	k_i	
$M(CO)_3D_3$ [C_{2v}]								
$Mo(CO)_3(PF_3)_3$	2075	1990	2015	Hyd.	16.61	16.56	0.29	*(173)*
$Mo(CO)_3(PCl_3)_3$	2056	~1963	~1963(?)	Hyd.	15.96	16.38	0.27(?)	*(254)*
$Mo(CO)_3(PEt_3)_3$	1952	1846	~1841	Hyd.	13.86	14.49	0.37	*(41b)*

Compound	cm^{-1}		Medium	F_{CO} *(76, 77)* md/Å		Ref.
	A_1	E		k_1	k_i	
$M(CO)_3D_3$ [C_{3v}]						
$Mo(CO)_3(PF_3)_3$	2065	2012	Hyd.	16.62	0.29	*(173)*
$Mo(CO)_3(PCl_3)_3$	2040	1991	Hyd.	16.27	0.27	*(254)*
$Mo(CO)_3(PCl_2\phi)_3$	2016	1943	$CHCl_3$	15.64	0.39	*(4)*
$Mo(CO)_3(PCl\phi_2)_3$	1977	1885	$CHCl_3$	14.83	0.48	*(4)*
$Mo(CO)_3(P\phi_3)_3$	1934	1835	Mull	14.10	0.50	*(254)*
$Mo(CO)_3(PEt_3)_3$	1937	1841	Hyd.	14.18	0.49	*(254)*
$Mo(CO)_3(CN\phi)_3$	1953	1924(?)	Hyd.	15.08	0.15	*(45)*
$Mo(CO)_3(Et_2S)_3$	1930	1826	CH_2Cl_2	13.99	0.53	*(83)*
$Mo(CO)_3$(thioacetamide)$_3$	1909	1798	THF	13.60	0.56	*(83)*
$Mo(CO)_3(NCCH_3)$	1915	1783	Mull	13.50	0.66	*(260)*
$Mo(CO)_3$(diglyme)	1905	1835	KBr	13.86	0.27	*(328)*
$Mo(CO)_3$(dien)	1898	1758	CH_3NO_2	13.13	0.73	*(197)*

TABLE II (*Continued*)

Compound	A_{2u} (cm^{-1})	Medium	Ref.
$M(CO)_2D_4$ [D_{4h}]			
$Mo(CO)_2(PF_3)_4$	1989	Hyd.	(*173*)

	cm^{-1}			F_{CO} (*76, 77*) md/Å		
Compound	A_1	B_1	Medium	k_1	k_i	Ref.
$M(CO)_2D_4$ [C_{2v}]						
$Mo(CO)_2(PF_3)_4$	2048	2010	Hyd.	16.59	0.29	(*173*)
$Mo(CO)_2(PCl_3)_4$	2018	—	Hyd.	—	—	(*254*)
$Mo(CO)_2[P(OMe)_3]_4$	1909	1856	Hyd.	14.30	0.41	(*254*)

	cm^{-1}		F_{CO} (*76, 77*) md/Å	
Compound	A_1	Medium	k_1	Ref.
$M(CO)D_5$ [C_{4v}]				
$Mo(CO)(PF_3)_5$	2029	Hyd.	16.61	(*173*)

---

[a] Hyd. = saturated hydrocarbon solvent.

[b] Estimated (*76*).

Under this interpretation, there is thus a small but real ability on the part of CN to accept metallic d_π electrons in competition with CO.

Additional assumptions as to the nature of bonding in metal carbonyls, in an attempt to demonstrate the internal consistency of the force constant–bond order relationship, however, are open to question, and thus the reliability of such calculations has not been satisfactorily demonstrated. Thus, for example, use of the relationship, employing the harmonic force constants of CO and $Mo(CO)_6$ (*179a, 179b, 180*), to estimate the number of electron pairs accepted by CO in $Mo(CO)_6$ gives a value of a 0.13 electron pair, compared with a value of 0.50 electron pair assumed by Cotton.

b. Metal-Carbon Stretching and M—C—O Deformation Modes. Metal-carbon stretching, and metal-carbon-oxygen deformation frequencies, as well as carbonyl stretching frequencies, should be quite sensitive to the net charge-releasing effects of substituent groups, since both the M—C and C—O bond orders are affected by the extent of metal-carbonyl $d_\pi—p_\pi^*$ interaction. Increases in δ_{MCO} and ν_{MC} with increasing ligand donating properties have been observed (*10, 254*). ν_{MC} frequencies (ca. 400 cm^{-1}) are relatively unimportant, however, since they obey the same selection rules as do the more readily interpretable ν_{CO}. The numbers of infrared-active MCO deformation modes for various $M(CO)_{6-x}D_x$ molecules are given in Table III. Difficulties in the study of MCO deformation modes may arise in that coupling of δ_{MCO} with ν_{MC} and other molecular vibrations of the same symmetries may become important, and in that ligand vibrations may occur in the δ_{MCO} region (500–700 cm^{-1}) and thus limit the applicability of the studies (*10, 254*). Poor agreement between the number of bands obtained and the number predicted, attributed to the accidental degeneracy of bands, has been obtained in the studies of δ_{MCO} thus far made. Metal-ligand stretching modes for the PF_3 derivatives of Ni are found ca. 200 cm^{-1}

TABLE III
M—C—O Deformation Modes for $M(CO)_{6-x}D_x$ Molecules

Structure	Symmetry	δ_{CO} Modes spanned	No. IR-active	No. Raman-active
$M(CO)_5D$	C_{4v}	$A_1 + A_2 + B_1 + B_2 + 3E$	4	6
trans-$M(CO)_4D_2$	D_{4h}	$A_{2g} + B_{2g} + E_g + A_{2u}$ $+ B_{2u} + E_u$	2	2
cis-$M(CO)_4D_2$	C_{2v}	$2A_1 + 2A_2 + 2B_1 + 2B_2$	6	8
trans-$M(CO)_3D_3$	C_{2v}	$A_1 + A_2 + 2B_1 + 2B_2$	5	6
cis-$M(CO)_3D_3$	C_{3v}	$A_1 + A_2 + 2E$	3	3
trans-$M(CO)_2D_4$	D_{4h}	$E_g + E_u$	1	1
cis-$M(CO)_2D_4$	C_{2v}	$A_1 + A_2 + B_1 + B_2$	3	4
$M(CO)D_5$	C_{4v}	E	1	1

(*335*), but none has been reported for the Group VIB derivatives. Despite the direct applicability of M—D stretching data to the problems of bonding in mixed complexes, it seems unlikely that they will be studied to any great extent.

2. Raman Spectra

Raman spectra are a useful complement to infrared data, but unfortunately many substituted metal carbonyls are poorly suited for Raman studies because of their sensitivity to oxygen and ultraviolet radiation, their low solubilities, and their tendency to isomerize or decay in solution (*254*). The few studies made, however, have confirmed, for example, the spectral assignments of the weak transition ca. 2000 cm^{-1} (Table II) and of the formally infrared-forbidden transitions observed for *trans* diphosphines (*77, 254*).

3. Ultraviolet and Visible Spectra

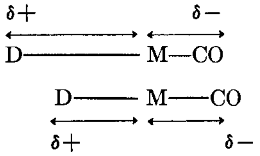
Although absorption maxima for ultraviolet and visible bands have been reported for a number of derivatives (Table IV, *et seq.*), little work has been done with regard to the systematic study and interpretation of such data.

Complexes $M(CO)_5D$ (D bonded through N or O) have absorption spectra consisting of two bands, a new high absorption band in the visible (~4000 Å; log ϵ_{max} 3.4–3.75) and a band at shorter wavelengths (~2500 Å; log ϵ_{max} 4.5–4.8) (*97, 290*). The bands are little affected by differences in donor or metal, and are probably characteristic of $D \rightarrow M(CO)_5$ complexes (*94, 290*). The spectrum of $(pip)_2W(CO)_4$ is similar, with extinction coefficients slightly reduced (*290*).

C. DIPOLE MOMENTS

Dipole moments for coordinately bonded Group VIB metal carbonyl substitution products have been given by several authors (Table IV, *et seq.*). Strohmeier and Langhauser (*307*) have reported dipole moments for derivatives of nitrogen, for most of which the donor is structurally unable to function as a π-acceptor. The data support the idea that the metal-donor partial bond moment for the monosubstitution products of a particular Group VIB metal remains essentially constant; dipole moments for *cis* disubstituted derivatives of the weakly π-accepting ligand, py, have been estimated with a fair degree of accuracy through the assumption that the metal-donor partial bond moments remain constant for the mono and *cis* disubstituted derivatives.

Bigorgne and Messier (*44a*) have investigated the dipole moments for derivatives of π-accepting ligands (P, As), using the dipole data of Chatt and Watson (*68*) and employing the assumption that the center of negative charge resides in the vicinity of the carbonyl carbon atom. Their results show that the partial positive charge on a π-accepting ligand decreases with increased displacement of CO groups. This observation is consistent with an increase in the π-accepting ability of the ligand with increased negative charge on the metal. Dipole moments for structurally analogous derivatives decrease with increased π-accepting ability of the ligand, and thus Eq. (3) may schematically represent the relative contributions of partial M—D and M—CO bond moments to the dipole moment of a derivative in the cases of (a) limited, and (b) extensive, displacement of CO by charge-releasing π-accepting ligands:



$$\begin{array}{ll} \overset{\delta+}{\longleftrightarrow} \quad \overset{\delta-}{\longleftrightarrow} & \\ \text{D}\text{———————M—CO} & \text{(a)} \\ \text{D————M———CO} & \text{(3)} \\ \underset{\delta+}{\longleftrightarrow} \quad \underset{\delta-}{\longleftrightarrow} & \text{(b)} \end{array}$$

D. The Derivatives

1. *Simple Derivatives,* $M(CO)_{6-x}D_x$

a. Preparation and Properties. Preparation of simple substitution products may be used to exemplify the several general preparative methods for mixed metal carbonyl complexes. There are, with variations, three basic routes to their synthesis:

(*i*) Direct displacement of CO from the carbonyl by a donating group. This may be accomplished by refluxing the metal carbonyl and ligand in an appropriate common solvent, or heating the reactants in a sealed tube or autoclave. More recently, strong ultraviolet radiation, from a mercury arc lamp for example, has been used to give smooth stepwise displacement of CO (*284*). The proper choice of method is usually dependent on the products desired, and upon the characteristics of the ligand; often conditions can be chosen to yield the desired product:

$$\text{Mo(CO)}_6 + \text{PF}_3 \xrightarrow[\Delta]{\text{autoclave}} \text{Mo(CO)}_{6-x}(\text{PF}_3)_x \qquad (4)$$

$T = 150°\text{–}185°$, $x = 1,2,3$
$T = 190°\text{–}300°$, $x = 3\text{–}5$
removal of CO, $x = 6$ (*173*)

$$\text{Mo(CO)}_6 + \text{NCCH}_3 \xrightarrow[h\nu \text{ or } \Delta]{} \text{Mo(CO)}_{6-x}(\text{NCCH}_3)_x \qquad (5)$$

solvent, *n*-hexane under CO atm, $x = 1$
solvent, *n*-hexane under N_2 stream, $x = 2$ precipitates
solvent, $NCCH_3$ under N_2, $x = 3$ (*95*)

(*ii*) Displacement of substituent groups from mixed complexes by the desired ligand. For acrylonitrile derivatives, direct displacement of CO was found to be too drastic to yield the desired products, so the corresponding acetonitrile derivative was used under milder conditions (*260*):

$$\mathrm{Mo(CO)_5(NCCH_3) + CH_2{=}CHCN \rightarrow Mo(CO)_5(NCCH{=}CH_2) + CH_3CN} \qquad (6)$$

The displacement of an aromatic or quasi-aromatic group or chelating ligand, e.g., mesitylene (*239*), cycloheptatriene (*4*), or diglyme (*328*), from a complex often provides a convenient route to a specific isomer, or to a higher substitution product not obtainable through direct displacement:

$$\text{piperazine} + \mathrm{Mo(CO)_6} \rightarrow \text{(piperazine)}\mathrm{Mo(CO)_5 + CO} \qquad (7)$$

(only product)

$$\text{piperazine} + \mathrm{MO(CO)_3(C_6H_5CH_3)} \rightarrow \text{(piperazine)}_3\mathrm{Mo(CO)_3 + C_6H_5CH_3}\ (\mathit{143}) \qquad (8)$$

The stereochemistry of a product cannot always be inferred in such displacement reactions. Thus displacement of CH_3CN from the *cis* trisubstituted derivative yields *trans*-$\mathrm{Mo(CO)_3(\pi{-}CH_2{=}CHCN)_3}$ (*260*).

(*iii*) The attack on carbonyl metallate ions by various donor groups will often produce mixed molecular complexes, e.g. (*30*):

$$\mathrm{[Cr(CO)_5]^{2-} + 2H_2O + py \rightarrow pyCr(CO)_5 + H_2 + 2OH^-} \qquad (9)$$

Simple mixed derivatives are typically yellow or white, diamagnetic, and soluble in common organic solvents; solubility in nonpolar solvents in general decreases with increased displacement of carbonyl groups. Typical means of purification include vacuum sublimation, column or vapor phase chromatography, and recrystallization. Table IV lists the simple substitution products $M(CO)_{6-x}D_x$ thus far reported.

b. Some Individual Complexes. Acetonitrile and acrylonitrile: Acetonitrile derivatives, and the mono- and disubstituted acrylonitrile complexes, are bonded through the lone pair on nitrogen, rather than through the CN triple bond, or, for acrylonitrile, through the olefinic linkage. In CH_3CN derivatives, the CN stretching frequencies are shifted to higher frequencies, in analogy to the upward shift observed for BF_3NCCH_3, for which bonding must be "end on" (*276*). The shift has been explained by Gerrard and co-workers (*147*) in terms of possible mesomerism which can diminish the bond order in the free nitrile, while different hybridization for bonded nitrile raises the CN bond order in the complexes. Acetonitrile is a slight π-acceptor in competition with CO (Section B,1*a*). "End on" bonding in mono- and disubstituted acrylonitrile derivatives is supported by the relatively high CN stretching frequencies for the complexes, the similarity in position of the C=C stretching frequencies, and only minor differences in the nuclear magnetic resonance (NMR) spectra for the complexes and the free nitrile

TABLE IV
COORDINATELY BONDED DERIVATIVES OF MONODENTATE LIGANDS

Donor group	M^a	n^b	Preparation^c	Physical measurements^d	Ref.
(A) Carbon					
$CNCH_3$	Cr, Mo	1, 2c, 3c	1, 2	1, 2, 3	(*42, 82, 159*)
$CN\phi$	Cr, Mo	1, 2c, 3c	1, 2	1, 2, 3	(*45, 159, 168*)
p-$CNC_6H_4CH_3$	Cr, Mo	3c	2	1, 2, 3	(*82, 159*)
p-$CNC_6H_4OCH_3$	Cr, Mo, W	1, 3c	1, 2	1, 2, 3, 4	(*159, 168*)
(B) Nitrogen					
$NCCH_3$	Cr, Mo, W	1, 2c, 3c	1, 2	1, 2, 3, 6	(*95, 260, 275, 289, 307, 315, 322*)
$NC\phi$	Cr	1	1	1, 2, 6	(*289, 307*)
$NCCH{=}CH_2$	Cr, Mo, W	1, 2c	2	1, 2, 3, 7	(*218, 260, 320*)
py	Cr, Mo, W	1, 2c, 3c	1, 2, 3	1, 2, 3, 4, 5, 6, 10	(*4, 25, 30, 35, 164, 166, 170, 197, 234, 287, 288, 290, 291, 293, 307*)
Me-pyrazine	Cr, Mo	2c	1	1, 3, 4	(*207*)
Urotropin	Mo	1	1	1, 3, 4	(*207*)
Aniline	Cr, Mo	1	1, 3	1, 2, 5, 6	(*31, 288, 291, 293, 307*)
NH_3	Cr, Mo, W	1, 2c, 3c	3	1, 3, 5	(*25, 26, 29, 30, 35, 157, 159, 163, 164, 230*)
pip	Cr, Mo, W	1, 2c	1	1, 2, 4, 6	(*290, 292, 307*)
quin	Cr, Mo	1	1	1, 2, 3, 4	(*206, 290*)
4-Aminopy	Mo	2c, 3c	1	1, 2	(*316*)
Morpholine	Cr, Mo, W	1, 2c, 3c	1, 2	1, 2, 3	(*143*)
Pyrrolidine	Mo, W	1, 2c	1	1, 2, 3	(*143*)
Cyclohexylamine	Cr, Mo, W	1	1	1, 2, 3	(*197*)
2-Me-pyrazine	Cr, Mo	2c	1	1, 2, 3, 4	(*206*)
p-$(NH_2)_2C_6H_4$	Mo, W	1, 2c	2, 3	1, 2	(*35, 316*)
α-Picoline	Cr	1	1	6	(*307, 309*)
2,6-Lutidine	Cr	1	1		(*309*)
γ-Cl-py	Cr	1	1	6	(*307, 309*)
Isoquin	Cr	1	1	6	(*307, 309*)
Isotropin	Cr	1	1		(*309*)
o-$(NH_2)_2C_6H_4$	Cr	1	3	1, 5	(*31*)
Piperazine	Mo	3c	2	1, 3	(*143*)
Et_3N	Cr, Mo, W	1, 2c	1	1, 2, 3	(*251, 292*)
$C_5H_{11}NH_2$	Mo	1	1	3	(*251a*)
$(C_5H_{11})_2NH$	Mo	1	1	3	(*251a*)
$(C_5H_{11})_3N$	Mo	1	1	3	(*251a*)

TABLE IV (*Continued*)

Donor group	M[a]	n[b]	Preparation[c]	Physical measurements[d]	Ref.
(C) Phosphorus					
PMe_3	Mo	1, 2t, 2c, 3t, 3c	1, 2	1, 2, 3	(*253, 254*)
PEt_3	Cr, Mo, W	1, 2t, 2c, 3t, 3c	1, 2	1, 2, 3, 8, 9	(*61, 177, 252, 253, 254*)
$P(n\text{-}Bu)_3$	Cr	1	1	1, 2	(*209*)
$P\phi_3$	Cr, Mo, W	1, 2t, 2c, 3c	1, 2, 3	1, 2, 3, 5, 9, 10	(*4, 30, 61, 162, 167, 197, 209, 221, 253, 254*)
$P(OMe)_3$	Mo	1, 2t, 2c, 3t, 3c, 4c	1, 2	2, 3, 9	(*253, 254*)
$P(OEt)_3$	Mo	1, 2t, 2c, 3t, 3c	1, 2	1, 2, 3, 9	(*253, 254*)
$POEt_3$	Mo	3c	1	1, 2, 3	(*61*)
$P(OBu)_3$	Cr	1, 2c	1	1, 2	(*209, 221*)
$P(O\phi)_3$	Cr, Mo, W	1, 2t, 2c, 3t, 3c	1, 2	1, 2, 3	(*209, 221, 253, 254*)
$PO\phi_3$	Mo, W	2c, 3c	1, 2	1, 2, 3	(*61*)
$P\phi Et_2$	Cr, Mo, W	2t, 2c, 3c	1, 2	1, 2, 3	(*61, 69*)
$P\phi_2Et$	Mo	3c	2	1, 2, 3	(*61*)
$PO\phi Et_2$	Mo	3c	1, 3	1, 2, 3	(*61*)
$PO\phi_2Et$	Mo	3c	1, 3	1, 2, 3	(*61*)
PCl_3	Cr, Mo, W	1, 2t, 2c, 3t, 3c, 4c	1, 2	1, 2, 3	(*4, 253, 254*)
$PCl_2\phi$	Mo	3c	2	1, 2, 3	(*4*)
$PCl\phi_2$	Mo	3c	2	1, 2, 3	(*4*)
PBr_2Me	Mo	1, 2c, 3c	1, 2	3	(*253, 254*)
$P(OEt)Cl_2$	Mo	1, 2c, 3c, 4c	1, 2	3, 9	(*253, 254*)
$P(CH_2CH_2CN)_3$	Cr	1	1	1, 2	(*209, 221*)
$P[N(CH_3)_2]_3$	Cr, Mo, W	1, 2t	1, 2	1, 2, 3, 7	(*183*)
$n\text{-}C_3H_7OPF_2$	Mo	3c	1, 2	1, 2, 3	(*262*)
$P(O\phi)F_2$	Mo	3c	2	1, 2, 3	(*262*)
$PF(O_2C_6H_4)$	Mo	3c	2	1, 2, 3	(*262*)
PF_2CH_2Cl	Mo	3c	2	1, 2, 3	(*261*)
$P[N(CH_3)_2]F_2$	Mo	3c	2	1, 2, 3	(*263*)
$P(NEt_2)F_2$	Mo	3c	2	1, 2, 3	(*263*)
$PF_2(pip)$	Mo	3c, 4c	2	1, 2, 3	(*263*)
PF_3	Mo	1, 2t, 2c, 3t, 3c, 4t, 4c, 5, 6	1, 2	1, 2, 3	(*76, 173, 198, 199, 200, 262*)
(D) Arsenic					
$AsEt_3$	Mo	1, 2t, 2c, 3c	1, 2	1, 3, 9	(*50*)
$As\phi_3$	Mo	1, 2c, 3c	1, 2, 3	1, 2, 3	(*4, 50, 162, 209, 221*)
$As(OMe)_3$	Mo	1, 2c, 3c	1, 2	1, 3	(*50*)
$AsCl_3$	Mo	1, 2c, 3c	1, 2	1, 3	(*4, 50*)
$As(NC_5H_{10})_3$	Mo	1, 2c	1	3	(*50*)

TABLE IV (*Continued*)

Donor group	M[a]	n[b]	Preparation[c]	Physical measurements[d]	Ref.
(E) Antimony					
$SbEt_3$	Mo	1, 2c, 3c	1, 2	1, 2, 3	(*38*)
$Sb\phi_3$	Mo	1, 2c, 3c	1, 2	1, 2, 3	(*4, 38, 209, 221*)
$Sb(OEt)_3$	Mo	—	—	—	(*38*)
$SbCl_3$	Cr, Mo	1, 3c	1, 2	1, 3	(*4*)
$SbClEt_2$	Mo	1, 2c	1	3	(*38*)
(F) Bismuth					
$BiEt_3$	Mo	1	1	3	(*38*)
$Bi\phi_3$	Mo	1, 2c	1	3	(*38*)
(G) Oxygen					
THF	Cr	1	1	1	(*291, 309*)
MF	Mo	1	1	1, 3	(*275*)
DMF	Mo, W	1, 2c	1	1, 3	(*275*)
$(CH_3)_2CO$	W	1	1	1, 3	(*275*)
EtOH	W	1	1	1, 3	(*275*)
n-$C_6H_{13}OH$	Mo	1	1	1, 3	(*275*)
$(i\text{-Bu})_2O$	Mo	1	1	1, 3	(*275*)
Et_2O	Mo, W	1	1	1, 3, 4	(*93, 97, 275*)
H_2O	Cr	3	3	1	(*158*)
(H) Sulfur					
SEt_2	Mo	1, 2c, 3c	1, 2	1, 2, 3	(*49, 82*)
SMe_2	Mo	3c	2	1, 3	(*81, 82*)
$S(CH_2)_4$	Mo	3c	2	1, 3	(*81, 82*)
$(NH_2)_2CS$	Mo	3c	2	1, 2, 3	(*81, 82*)
NH_2CSCH_3	Mo	1, 3c	1, 2	1, 2, 3	(*82, 318*)
$S\phi_2$	Mo	1	1	1, 3	(*174*)
DMSO	Mo	3c	3	1	(*162*)
(I) Selenium					
$Se\phi_2$	Mo	1	1	1, 3	(*174*)
(J) Halogens					
I	Cr	1	3	1, 5	(*37*)

Key to symbols used in Table IV, *et seq.*:

[a] Metal.

[b] Number and orientation of ligands, e.g., 2c = *cis*-$M(CO)_4D_2$.

[c] Preparation: 1—directly from carbonyl; 2—indirectly, through another molecular derivative; 3—indirectly through carbonyl metallate ion.

[d] Physical measurements: 1—color; 2—m.p.; 3—infrared; 4—ultraviolet–visible; 5—magnetic susceptibility; 6—dipole measurement; 7—NMR; 8—X-ray crystal data; 9—Raman spectrum; 10—conductivity data; 11—optical rotation; 12—electron-spin resonance.

(*219, 260, 265, 320*). In the complex *trans*-$Mo(CO)_3(CH_2{=}CHCN)_3$, bonding is through the C—C double bond (Section IV,E).

Pyridine derivatives: py, unlike aliphatic amines, possesses potentially π-accepting p_π orbitals partially delocalized on the ring, which are, however, anisotropic with respect to π-bonding. There are two possible orientations of the py ring in $M(CO)_5py$; for both arrangements the molecule has the same symmetry (Fig. 11). Only for structure (11a), however, can the ring accept metallic charge. The near identity of CO stretching frequencies and force constants for $Mo(CO)_5py$ and $Mo(CO)_5(NH_2C_6H_{11})$ (Table II) is consistent with structure (11b). For the *cis*-$M(CO)_4py_2$ derivatives, however, CO stretching frequencies and force constants (Table II) do indicate π-bonding (*197*).

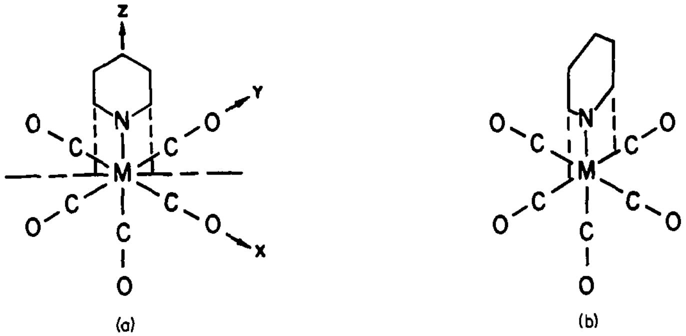
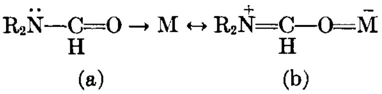


FIG. 11. The two symmetrical orientations of the pyridine ring in $M(CO)_5py$. Both forms have C_{2v} symmetry [from Kraihanzel and Cotton (*197*)]. (a) and (b): see text.

Derivatives of thiourea, thioacetamide, methylformamide, and dimethylformamide: Mixed derivatives of thiourea, thioacetamide, MF, and DMF all have anomalously low CO stretching frequencies, those for DMF being the lowest thus far reported for mono- and disubstituted complexes (Table II). Cotton (*76*) has interpreted the data for MF and DMF derivatives on the basis of the symmetry factorability of σ- and π-bonding in octahedral complexes (Section A,4) as indicating that MF and DMF are actually π-donors in these complexes. Thus there is postulated a small contribution of canonical form (10b) to a resonance hybrid description of the bonding:



$$\underset{(a)}{R_2\ddot{N}-\underset{H}{C}=O \rightarrow M} \leftrightarrow \underset{(b)}{R_2\overset{+}{N}=\underset{H}{C}-O=\overset{-}{M}} \qquad (10)$$

Conversely, disregarding the symmetry factoring approximation, the low frequencies may be attributed to enhanced D → M σ-donation, resulting from delocalization of the lone pair on nitrogen.

TABLE V
SUBSTITUTION PRODUCTS OF POLYDENTATE LIGANDS

(A) Compounds M(CO)$_{6-2x}$D$_x$

Compound	M^a	Color^b	M.P.^{b} (°C)	Preparation^a	Physical measurements^a	Ref.
(1) Nitrogen						
M(CO)$_4$(phen)	Cr, Mo, W	Red	—	1, 3	3	(*4, 28, 30, 166, 170*)
cis-M(CO)$_2$(phen)$_2$	Mo, W	Blue-black	—	1	3, 5	(*28*)
M(phen)$_3$	Cr, Mo, W	Black	—	1^c		(*28*)
M(CO)$_4$(dipy)	Cr, Mo, W	Red	—	1, 3	3, 5, 10	(*4, 28, 170, 197, 206, 271*)
cis-M(CO)$_2$(dipy)$_2$	Mo, W	Red-violet	—	1	3	(*28*)
M(dipy)$_3$	Cr, Mo, W	Black	—	1^c		(*28*)
M(CO)$_4$(en)	Cr, Mo, W	Yellow	294 dec	1, 3	3	(*30*)
M(CO)$_4$(8-aminoquinoline)	Cr	Yellow-brown	>150 dec	1	3	(*206*)
M(CO)$_4$[(C$_5$H$_5$N)$_2$CH$_2$]	Mo	—	>150 dec	1	4	(*206*)
M(CO)$_4$[(C$_4$H$_4$N)$_2$CH$_2$]	Mo	—	>150 dec	1	4	(*206*)
M(CO)$_4$(cyclohexane-1,2-diamine)	Cr	Yellow	—	3	5, 10	(*31*)
M(CO)$_4$[(C$_4$H$_8$N)$_2$CH$_2$]	Mo	—	—	1	4	(*206*)
M(CO)$_4$[(C$_5$H$_{10}$N)$_2$CH$_2$]	Mo	—	—	1	4	(*206*)
M(CO)$_4$[(Et$_2$N)$_2$CH$_2$]	Mo	Yellow	>150 dec	1	4	(*206*)
M(CO)$_4$[(Me$_2$N)$_2$C$_2$H$_4$]	Cr, Mo, W	Yellow	—	1	3	(*251a*)
(2) Phosphorus						
M(CO)$_4$[C$_2$H$_4$(PEt$_2$)$_2$]	Cr, Mo, W	White	106.5–107	1	3, 10	(*10, 68*)
M(CO)$_4$[*o*-C$_6$H$_4$(PEt$_2$)$_2$]	Cr, Mo, W	White	181.5–182	1	3, 6, 10	(*10, 68*)
cis-M(CO)$_2$[*o*-C$_6$H$_4$(PEt$_2$)$_2$]$_2$	Cr, Mo, W	Yellow	257–258	1	3, 6, 10	(*10, 68*)

$M(CO)_4[C_2H_4(P\phi_2)_2]$	Cr, Mo, W	White	193–194	1	3	(*68, 338*)
$M(CO)_4[C_6H_4(P\phi_2)_2]$	Cr, Mo, W	White	193–194	1	3, 10	(*10, 68, 338*)
$M(CO)_4[CH_2(P\phi_2)_2]$	Cr, Mo, W	Yellow	195.5–196	1	3, 10	(*10, 68*)
cis-$M(CO)_2[CH_2(P\phi_2)_2]_2$	Cr, Mo, W	Yellow	324–325	1	3, 6, 10	(*68*)
trans-$M(CO)_2[CH_2(P\phi_2)_2]_2$	Cr	Vermilion red	279–280	1	3, 6, 10	(*68*)
cis-$M(CO)_2[C_2H_4(P\phi_2)_2]_2$	Cr, Mo, W	Yellow	263 dec	1	3	(*10, 338*)
(3) Arsenic						
$M(CO)_4$(diars)	Cr, Mo, W	White	158	1	3, 5, 10	(*18, 240, 241*)
cis-$M(CO)_2$(diars)	Cr, Mo, W	Yellow	231	1	3, 5, 10	(*18, 240, 241*)
$M(CO)_4[C_2H_4(As\phi_2)_2]$	Cr, Mo, W	White	176	1	3	(*339*)
cis-$M(CO)_2[C_2H_4(As\phi_2)_2]_2$	Cr, Mo	Yellow	252	1, 2	3	(*339*)
(4) Sulfur						
$M(CO)_4$(DTH)	Cr, Mo, W	Yellow	148 dec	1	3, 7	(*213*)
$M[S(\phi)C = C(\phi)S]_3$	Cr, Mo, W	—	>360 dec	1	—	(*266*)
$M[S(F_3C)C = C(CF_3)S]_3$	Cr, Mo, W	Purple	>245	1	3, 7, 5, 12	(*89a, 182*)
(5) Oxygen						
$M(aca)_3$	Cr, Mo, W	Olive green	228	1	3	(*148*)

(B) Compounds $M(CO)_{6-3x}D_x$

(1) Nitrogen						
$M(CO)_3$(tripy)	Mo, W	—	—	1	3	(*24*)
$M(tripy)_2$	Mo, W	Permanganate		1		(*24*)
$M(CO)_3$(dien)	Cr, Mo, W	Yellow	dec > 230	1, 2	3	(*4, 197, 228*)
$M(CO)_3$(trien)	Mo	Yellow	204–205	1	3	(*259a*)
$M(CO)_3(CH_2—N—RCH_2—N—RCH_2—N—R)$						
$R = CH_3$	Cr, Mo	Yellow	dec > 150	1, 2	3	(*206*)
$R = C_2H_5$	Cr, Mo	Yellow	dec > 150	1, 2	3	(*206*)
$R = C_6H_{11}$	Cr, Mo	Yellow	dec > 150	1, 2	3	(*206*)

TABLE V (*Continued*)

(A) Compounds $M(CO)_{6-2x}D_x$

Compound	M[a]	Color[b]	M.P.[b] (°C)	Preparation[a]	Physical measurements[a]	Ref.
(2) Phosphorus						
$M(CO)_3[\phi P(o\text{-}C_6H_4PEt_2)_2]$	Mo	Pale yellow	268.5–269	1	3, 10	(*68*)
$M(CO)_3[\phi P(C_2H_4P\phi_2)_2]$	Mo	White	261.5–263	1	3, 10	(*68*)
$M(CO)_3[Me{\cdot}C(CH_2P\phi_2)_3]$	Cr, Mo, W	White	378–380 dec	1	3, 6, 10	(*68*)
(3) Arsenic						
$M(CO)_3$(triars)	Cr, Mo, W	Yellow	—	1, 2	3, 5, 10	(*217*)
(4) Oxygen						
$M(CO)_3$(diglyme)	Mo	Yellow	156–160 dec	1	3	(*328*)
(5) Sulfur						
$M(CO)_3$(TTU)	Cr, Mo	Off-white	145	1	3, 7	(*213*)

[a] See key to symbols (Table IV).

[b] Of Mo derivative.

[c] Also prepared directly from Group VIB metal halides (*156*).

Derivatives of PF_3: Clark and Hoberman have recently prepared the complete series of PF_3 substituted Group VIB carbonyls (*173*). Preliminary examination of the infrared data for these derivatives indicates that PF_3 very closely approaches CO in both its donating and accepting ability; thus it is not unlikely that an entire new series of zerovalent substitution products, those of PF_3, will be the subject of extensive investigation in the future.

2. Derivatives of Polydentate Ligands

Table V gives information about simple mixed complexes of di- and tridentate ligands, and one complex of a tetradentate group. For the latter, in keeping with the difficulty of breaking metal-carbon bonds in more highly substituted derivatives, only three carbonyls are displaced. The derivative has one free amine group, and thus is readily soluble in dilute HCl to give a hydrochloride (*259a*). Behrens and coworkers (*24, 28*) have recently succeeded in completely displacing CO from the hexacarbonyl with dipy and tripy. The preparation of these derivatives have dispelled a widely held belief that only for coordinating groups which approach CO in π-accepting ability could complete displacement occur in the Group VIB metal carbonyls. Thus it appears likely that complete displacement of CO with most polydentate ligands, bonding for example through P or As, can be achieved.

3. Mixed Derivatives, $M(CO)_3XY$

Highly colored mixed complexes of the general type $M(CO)_3XY$, where X is phen or dipy, have been prepared through the direct displacement of

TABLE VI
DERIVATIVES OF TYPE $M(CO)_3XY$

Compound	Color	Preparation[a]	Physical measurements[a]	Ref.
$Cr(CO)_3NH_3$	Black	1	3, 10	(*29*)
$Mo(CO)_3(dipy)NH_3$	Dark red	1	3	(*29*)
$W(CO)_3(dipy)NH_3$	Blue-violet	1	3	(*29*)
$Cr(CO)_3(phen)NH_3$	Blue-black	1	3, 10	(*29*)
$Mo(CO)_3(phen)NH_3$	Black-brown	1	3, 5	(*29*)
$W(CO)_3(phen)NH_3$	Blue-violet	1	3	(*29*)
$Mo(CO)_3(dipy)(py)$	Deep red	1	3, 10	(*272*)
$W(CO)_3(dipy)(py)$	Black	1	3	(*29*)
$Cr(CO)_3(phen)(py)$	Red-black	1	—	(*166*)
$Mo(CO)_3(phen)(py)$	Red-black	1	—	(*166*)
$W(CO)_3(phen)(py)$	Almost black	1	—	(*170*)
$Mo(CO)_3(dipy)(\phi_3P)$	Purple	1	3, 10	(*272*)
$Mo(CO)_3(dipy)(\phi_2S)$	Brown	1	3, 10	(*272*)

[a] See key to symbols (Table IV).

CO from the parent $M(CO)_4X$ complexes. Their properties are listed in Table VI. The mixed derivatives are prepared under milder conditions than are required for the formation of any bis-chelated derivatives thus far reported (*28*, *272*). The ease of preparing them may be explained in terms of the stronger M—C bonding *trans* to a charge-releasing substituent (Section II,A); in order for a second bidentate group to be introduced one such bond would necessarily have to be broken, while a monodentate ligand might still enter *trans* to a CO to give the *sym* trisubstitution product (*272*).

4. Hepta-Coordinated Halogen Derivatives

a. Preparation and Properties. Carbonyl derivatives of bi- and tridentate ligands bonding through N, As, or S yield a variety of yellow or orange oxidation products when treated with Br_2 or I_2 in an inert solvent. The oxidations may be conveniently followed spectrophotometrically by noting the sharp increase in free halogen concentration at the stoichiometric point (*242*) (Fig. 12). Properties of the mononuclear derivatives are listed in Table VII; the dimeric products are discussed below in subsection 5.

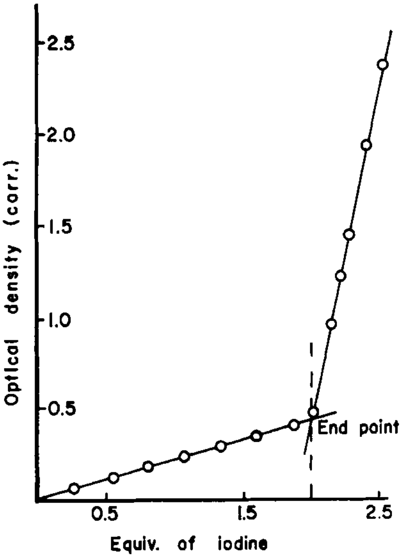


FIG. 12. Spectrophotometric titration of Mo(diars)$(CO)_4$ with iodine in CCl_4 (λ = 500 mμ; 1-cm cell) [from Nigam *et al.* (*242*)].

b. Stereochemistry and Bonding. The stoichiometry of the derivatives, together with infrared and magnetic susceptibility data, suggests that many of the carbonyl derivatives may be formulated as low symmetry hepta-coordinated complexes of the di- or trivalent metal atom. It has been proposed, for example, that complexes of the type $M(CO)_3(bidentate)X_2$ are pentagonal bipyramidal, with the electronegative halogen atoms attached through the longer axial bonds (*242*) (Fig. 13). Distortion of the pentagonal bipyramid should result from the nonidentity of the seven coordinating groups, and from steric effects in the equatorial plane. The unusual coordination number for these complexes has been explained in terms of the generalized case of Sidgwick's rule: the transition metal ion tends to make use of all nine valence orbitals (*242*). For a metal ion with four or fewer spin-paired nonbonding valence electrons, as can be the case for Group VIB metals of oxidation state ≥ 2, seven-coordination is therefore possible. Spin pairing is most likely for a complex in which the ligand field is great, e.g., when double bonding between metal and ligand is important. Interelectronic repulsions are smaller for ions in the second and third transition series, and the ability of the Group VIB metals to form hepta-coordinated derivatives might therefore be expected to be greater for Mo and W than for Cr (*242*). Thus, for example, whereas treatment of $Cr(CO)_5I^-$ with I_2 yields the paramagnetic $Cr(CO)_5I$ (*37*), the same reaction with Mo or W gives salts of $M(CO)_4I_3^-$ (*185*).

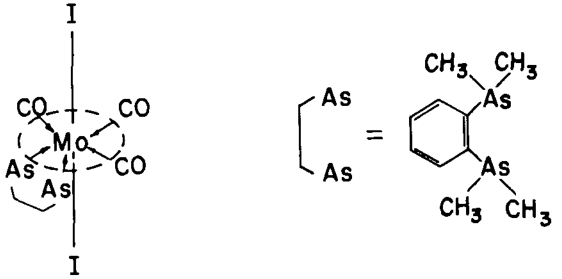


FIG. 13. The proposed structure of $(diars)Mo(CO)_3I_2$ [from Nigam *et al.* (*242*)].

While displacement of carbonyl groups in bis diarsine derivatives cannot be effected, presumably because of the stronger M—C bonds engendered by the charge-releasing chelate groups, the ease of displacement of CO from mono diarsine derivatives to yield non-carbonyl-containing six-coordinated products increases in the order W < Mo < Cr. It has been proposed that the greater inaccessibility of *d* orbitals in Cr than in Mo or W, which renders hepta-coordination utilizing three of them more difficult, also contributes to the instability of hepta-coordination in Cr relative to that for Mo and W (*201*).

Reaction of SO_3 with $Mo(CO)_6$ (in liquid SO_3) has led to hepta-coordinated, probably polymeric $Mo(CO)_4O(SO_3)_2$, believed to have three metal-oxygen bonds (*327*).

TABLE VII
HEPTA-COORDINATE AND RELATED DERIVATIVES OF GROUP VIB METAL CARBONYLS

Complex	Color	M.P.	μ_{eff} (solid at 20°C)	Molecular conductivity Ω^{-1} cm^2 (10^{-3} M in ϕNO_2)	Ref.
$[Mo(CO)_3(dipy)Br_2]$	Deep yellow	—	Diamagnetic	0.25	*(271)*
$[W(CO)_3(dipy)Br_2]$	Deep yellow	—	Diamagnetic	0.27	*(271)*
$[W(CO)_3(dipy)I_2]$	Orange	—	Diamagnetic	0.28	*(271)*
$[W(CO)_3(dipy)(HgCl)_2]$	Orange	—	Diamagnetic	Nonconductor	*(146a)*
$[Cr(diars)Br_3(H_2O)]^a$	Blue	—	3.85	1.5	*(201)*
$[Cr(CO)_2(diars)_2Br]Br$	Pale yellow	—	Diamagnetic	22.7	*(201)*
$[Cr(CO)_2(diars)_2Br]Br_3$	Yellow	—	Diamagnetic	26.2	*(201)*
$[Cr(CO)_2(diars)_2I]I$	Deep orange	—	Diamagnetic	25.8	*(201)*
$[Cr(CO)_2(diars)_2I]I_3$	Brown	—	Diamagnetic	29.5	*(201)*
$[Cr(diars)_2I_2]I_3{}^a$	Dark green	—	3.83	26.1	*(201)*
$[Mo(CO)_3(diars)Br_2]$	Deep orange	dec > 200°	Diamagnetic	2.2	*(242)*
$[Mo(CO)_3(diars)I_2]$	Golden yellow	dec > 200°	Diamagnetic	1.2	*(242)*
$[Mo(CO)_2(diars)I_2]^a$	Deep orange	—	1.98	1.5	*(201)*
$[Mo(CO)_2(diars)I_3]$	Dark brown	—	1.40	1.6	*(201)*
$[Mo(diars)Br_4]^a$	Orange brown	210° dec	1.96	11.6	*(242)*
$[Mo(CO)_2(diars)_2Br]Br$	Pale yellow	200° dec	Diamagnetic	23.5	*(242)*
$[Mo(CO)_2(diars)_2Br]Br_3$	Deep yellow	210° dec	Diamagnetic	20.5	*(242)*
$[Mo\ (CO)_2(diars)_2I]I$	Pale yellow	195° dec	Diamagnetic	27.4	*(242)*
$[W(CO)_4(diars)I]I$	Orange	—	Diamagnetic	27.3	*(202)*
$[W(CO)_4(diars)I]I_3$	Deep orange	—	Diamagnetic	25.0	*(202)*
$[W(CO)_3(diars)Br_2]$	Yellow	—	Diamagnetic	2.1	*(202)*
$[W(CO)_3(diars)Br_2]Br$	Yellow-green	—	1.54	24.0	*(202)*
$[W(CO)_2(diars)_2Br]Br$	Yellow	—	Diamagnetic	24.3	*(202)*
$[W(CO)_2(diars)_2Br]Br_3$	Deep yellow	—	Diamagnetic	28.1	*(202)*

$[W(CO)_2(diars)_2I]I$	Deep yellow	—	Diamagnetic	26.4	(*202*)
$[W(CO)_2(diars)_2I]I_3$	Deep orange	—	Diamagnetic	27.2	(*202*)
$[Mo(CO)_3(DTH)Br_2]$	Orange	125° dec	—	—	(*213*)
$[Mo(CO)_3(DTH)I_2]$	Dark orange	40° dec	—	—	(*213*)
$[W(CO)_3(DTH)Br_2]$	Orange	145° dec	—	—	(*213*)
$[W(CO)_3(DTH)I_2]$	Pale orange	135° dec	—	—	(*213*)
$[Mo(CO)_2(triars)X_2]$	—	—	—	—	(*217*)
$[W(CO)_3(triars)X]X$	—	—	—	—	(*217*)
$[Mo(CO)_4(O(SO_3)_2)]$	Yellow	(dec)	Diamagnetic	—	(*327*)
$[Mepy][Mo(CO)_4I_3]$	Yellow	—	—	Ionic	(*185*)
$[Mepy][W(CO)_4I_3]$	Yellow	—	—	Ionic	(*185*)

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[a] Hexa-coordinate derivatives.

TABLE VIII
POLYNUCLEAR DERIVATIVES OF THE GROUP VIB CARBONYLS

Compound	Color	M.P.	Preparation^a	Physical properties^a	Ref.
N-Bridged					
m-Phenylenediamine$[Cr(CO)_5]_2$	Yellow	dec	3	5, 10	(*31*)
p-Phenylenediamine$[Cr(CO)_5]_2$	Yellow	dec > 150°	3	10	(*31*)
1,3,5-Triaminobenzene$[Cr(CO)_5]_3$	Yellow	dec > 75°	3	10	(*31*)
Piperazine$[Mo(CO)_5]_2$	Yellow	—	1	3	(*143*)
Piperazine$[W(CO)_5]_2$	Yellow	—	1	3	(*143*)
$(CO)_3Cr(en)_3Cr(CO)_3$	Bright yellow	—	3	—	(*169*)
$(CO)_3Mo(en)_3Mo(CO)_3$	Yellow	—	3	—	(*162, 166*)
P-Bridged					
$P_2Me_4[Cr(CO)_5]_2$	Pale yellow	129°–132°	1	3, 4, 6, 7	(*65, 154*)
$P_2Me_4[Mo(CO)_5]_2$	Colorless	143°–144°	1	3, 4, 6, 7, 8	(*65, 66*)
$P_2Me_4[W(CO)_5]_2$	Colorless	162°–164°	1	3, 4, 6, 7	(*65, 66, 154*)
$(PMe_2)_2[Cr(CO)_4]_2$	Red	302°–303°	1	3, 4, 6, 7	(*65, 66, 154*)
$(PMe_2)_2[Mo(CO)_4]_2$	Orange	228°	1	3, 4, 6, 7	(*65, 154*)
$(PMe_2)_2[W(CO)_4]_2$	Orange	205°	1	3, 4, 6, 7	(*65, 154*)
$(PEt_2)_2[Cr(CO)_4]_2$	Maroon	No m.p. to 350°	1	3, 6	(*66*)
$(PEt_2)_2[Mo(CO)_4]_2$	Orange	dec > −30°	1	3, 6	(*66*)
$(PEt_2)_2[W(CO)_4]_2$	Orange	146°–149° dec	1	3, 6	(*66*)
$(P\phi_2)_2[Mo(CO)_4]_2$	Orange	290°–305°	1	3, 8	(*66*)
$(P\phi_2)_2[W(CO)_4]_2$	Red	No m.p. to 350°	1	3, 8	(*66*)
$P_2Et_4[Mo(CO)_5]_2$	Colorless	157°–159° dec	1	3, 6, 8	(*66*)
$P_2Et_4[W(CO)_5]_2$	Colorless	188°–189°	1	3, 6	(*66*)
$(PMe_2)_2[Mo(CO)_2Cp]_2$	Orange	dec 210°	1	3, 7	(*153*)
$(PMe_2)[Mo(CO)_2Cp]_2H$	Red-orange	215	3	3, 7, 8	(*95a, 153*)
$(\phi_2P)_3[Mo(CO)Cp]_3$	Dark green	336°–343° dec	1	3	(*153*)
$[C_2H_4(P\phi_2)_2]_3Cr_2(CO)_6$	Yellow	263° dec	1	3	(*338*)

$[C_2H_4(P\phi_2)_2]_3Mo_2(CO)_6$	Colorless	210° dec	1	3	*(61, 338)*
$[C_2H_4(P\phi_2)_2]_3W_2(CO)_6$	Yellow	194° dec	1	3	*(61, 338)*
$[C_2H_4(OP\phi_2)_2]_3Mo_2(CO)_6$	Pale yellow	245° dec	1	3	*(61)*
$[C_2H_4(OP\phi_2)_2]_3W_2(CO)_6$	Pale yellow	260° dec	1	3	*(61)*
$[CH_3SMo(CO)_2Cp]_2$	Black	130°	1	3, 7	*(323)*
$[CH_3SW(CO)_2Cp]_2$	Dark red	187°	1	3, 7	*(323)*
As-Bridged					
$(AsMe_2)_2[Mo(CO)_4]_2$	Orange	290°	1	3, 6, 7	*(66, 154)*
$(AsMe_2)_2[W(CO)_4]_2$	Orange	219°–221°	1	3, 6, 7	*(66, 154)*
$(As\phi_2)_2[Mo(CO)_4]_2$	Orange	277°–279° dec	1	3, 8	*(66)*
$As_2Me_4[Mo(CO)_5]_2$	Yellow	116.5°–117.5°	1	3, 6	*(66)*
$As_2Me_4[W(CO)_5]_2$	Yellow	144°–146°	1	3, 6	*(66)*
$[As(CF_3)_2]_2[Mo(CO)_2Cp]_2$	Brown	320°–330° dec	1	3, 7	*(87)*
$(AsMe_2)_2[Mo(CO)_2Cp]_2$	Dark red	309°–310° dec	1, 3	3, 7	*(153)*
$As_2Me_4[Cr(CO)_5]_2$	Pale yellow	108°–110°	1	3, 7	*(154)*
$(As_2Me_4[Cr(CO)_4])_m$	Yellow-orange	230° dec	1	3	*(154)*
$(As_2Me_4[Mo(CO)_4])_m$	Pale yellow	235° dec	1	3	*(154)*
$[C_2H_4(As\phi_2)_2]_3Mo_2(CO)_6$	White	228°	1	3	*(339)*
$[C_2H_4(As\phi_2)_2]_3W_2(CO)_6$	White	268°	1	3	*(339)*
S-Bridged					
$[(CH_3S)_2MoCp]_2$	Brown	—	1	3, 5, 7	*(184)*
$(CH_3S)_3Cr_2Cp_2$	Purple	—	1	3, 5, 7	*(184)*
$([SC(CF_3){=}C(CF_3)S]CrCp)_2$	Purple-brown	—	1	3, 7	*(184)*
$([SC(CF_3){=}C(CF_3)S]MoCp)_2$	Purple-brown	—	1	3, 5, 7	*(184)*
Halogen-Bridged					
$[Mo(CO)_3(dipy)I_2]_2$	Orange-brown	—	1	3, 5, 10	*(271)*
$[Cr(diars)Br_3]_2$	Green	—	1	5, 10	*(201)*
$[Mo(DTH)(CO)_2I]_2$	Red-brown	—	1	3	*(213)*
$(CO)_5CrICr(CO)_5$	Red	—	3	3, 5	*(34)*

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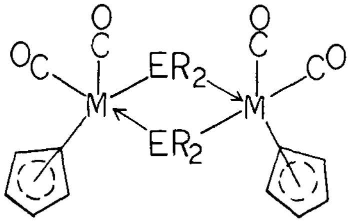
[a] See key to symbols (Table IV).

5. *Polynuclear Derivatives*

Data on polynuclear derivatives of the Group VIB carbonyls is given in Table VIII.

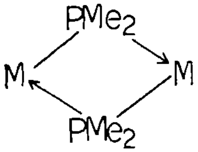
a. Nitrogen-Bridged. Reaction of $Cr(CO)_5^{2-}$ with the appropriate amine gives $(CO)_5CrNH_2C_6H_4NH_2Cr(CO)_5$ *meta* or *para*, whereas attempts to obtain the analogous *ortho* derivative yielded only the monosubstitution product $H_2NC_6H_4NH_2Cr(CO)_5$, presumably because of steric effects and the marked decrease in basicity of the second amino group (*31*). Similar binuclear bridged derivatives of piperazine have been prepared directly (*143*). Direct reaction of *p*-phenylenediamine with $Mo(CO)_6$ produces a complex in which only one N is bonded (*316*). Hexahydro-*o*-phenylenediamine, in which the second amino group is more basic than in the corresponding aromatic compound, reacts to form chelated derivatives, analogous to those of, for example, diars (*31*). Reaction of 1,3,5-phenylenetriamine with the $Cr(CO)_5^{2-}$ anion produces the trinuclear complex $C_6H_3(NH_2)_3(Cr(CO)_5)_3$ (*31*), while treatment of the base reaction product $(CO)_3Mo(OH)_3Mo(CO)_3^{3-}$ with en gives the dimeric derivative $(CO)_3$-$Mo(en)_3Mo(CO)_3$ (*162*).

b. P- or As-Bridged. A variety of polynuclear metal carbonyl complexes with bridging P or As groups, of which those of the Group VIB metals are representative, have recently been reported. Direct reaction of $[CpMo(CO)_3]_2$ with alkyl diphosphines or diarsines R_4E_2 has yielded bridged complexes (11) which have been shown by infrared data to contain *cis* carbonyl groups (*154*). The NMR spectrum of the Me_4P_2 derivative shows a 1:2:1 triplet characteristic of the



(11)

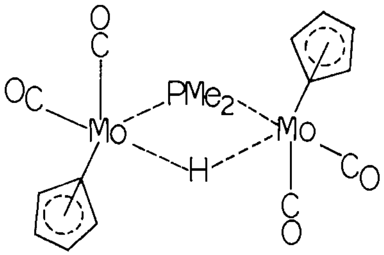
grouping, which has been interpreted as arising from P—P coupling in the ring (*153*). The same reaction with tetrakis(trifluoromethyl)diarsine gives,



(12)

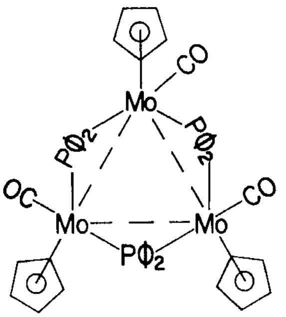
instead, the monomeric $CpMo(CO)_3[As(CF_3)_2]$, which may, however, be dimerized with CO loss through exposure to a strong ultraviolet source (*87*). The difference in chemical behavior between the trifluoromethyl and methyl derivatives has been attributed to the weakening of the charge-donating power of As by the strongly electronegative F_3C groups.

Reaction of $NaCpMo(CO)_3$ with $PClMe_2$ yields (13)

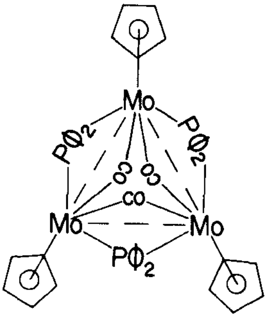


(13)

$[Cp_2Mo_2HP(CH_3)_2(CO)_4]$, which was identified by the similarity of its NMR spectrum to that of analogous Fe complexes (*153*). The origin of the H is as yet unexplained. A recent X-ray crystallographic investigation (*95a*) has confirmed structure (13). Although the position of the H was not explicitly verified, the similarity of environment for the two halves of the molecule strongly supports an equal association of the H with each. A bent three-center Mo—H—Mo bond involving one electron from the two Mo atoms and one electron from H has been proposed to account for the diamagnetism of the complex (*95a*). Postulation of a metal-metal bond is thus unnecessary. Reaction of $[CpMo(CO)_3]_2$ with tetraphenyl diphosphine results in the formation of a trimer instead of the expected dimeric product (*153*). The infrared spectrum in Nujol shows one CO stretching peak at 1852 cm^{-1}, which could be interpreted as arising from either bridging or terminal carbonyl groups. Low solubility of the complex precluded NMR studies, other than to confirm the diamagnetism of the complex, and thus the two structures (14) and (15) are consistent with chemical analysis. It appears more likely



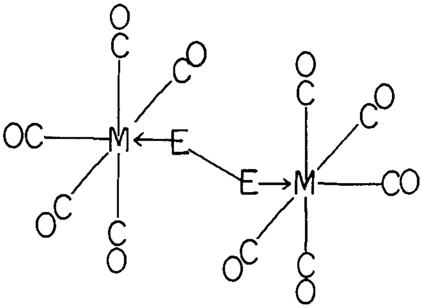
(14)



(15)

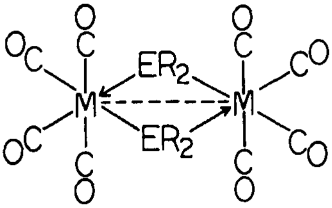
that the complex contains terminal carbonyl groups, if only because no Group VIB metal carbonyl complexes containing bridging carbonyl groups have yet been reported.

Simple displacement of carbonyl groups by tetraalkyl diphosphines or diarsines under reflux conditions or in sealed tubes has led to the synthesis of two distinct types of air- and moisture-stable bridging complex (*65*, *66*, *153*). At lower temperatures (180°–200°), colorless to yellow complexes of



(16)

type (16) are formed, while, at higher temperatures (240°–260°), rupture of the E—E bond results in the formation of orange to red complexes, (17), analogous to the Cp derivatives mentioned above. Here it is necessary



(17)

to postulate a metal-metal bond to account for the diamagnetism of the complexes. Tetraaryl diphosphines do not readily yield the second type of complex (*66*). Infrared spectra of the CO stretching region for the two complexes are quite similar to those for $M(CO)_5D$ and *cis*-$M(CO)_4D_2$. Dipole moments for the second type are about 1 D, indicating a slight asymmetry, produced, it has been argued, by a slight folding of the M—E—M bonds (Fig. 14). Such distortion could facilitate metal-metal bond formation, but could be limited by steric hindrance of the CO groups perpendicular to the plane containing the two P atoms. For analogous Fe complexes in which these CO groups are not present, folding is more pronounced, with dipole moments of about 4 D (*66, 88*). Independent NMR studies have demonstrated the nonequivalency of the four methyl groups (*153*).

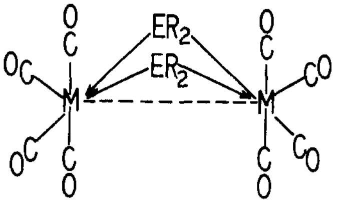
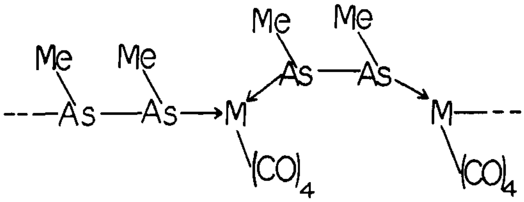


FIG. 14. Proposed structure for $[M(CO)_4PR_2]_2$.

For the first type of complex, dipole measurements have indicated that there is free rotation about the E—E bond (*66*).

In some reactions of this type, relatively insoluble products are obtained. Purification and analysis of the tetramethyldiarsine Cr and Mo complexes indicate that the materials are polymeric, of stoichiometry $[M(CO)_4As_2(Me)_4]_n$, with $n = 13$ for Cr, and about 20 for Mo. The structures have been postulated as



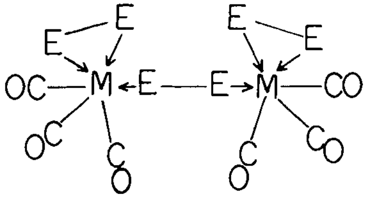
(18)

where terminal groups might be either $M(CO)_5$ or $As(Me)_3$ (*153*).

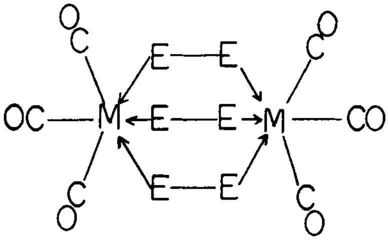
Reactions of diphenylphosphinic acid with $Cr(CO)_6$ result in CO-containing polymeric products, stable at 360°C (*250a*). It is difficult to believe that the structures proposed for these polymers are correct, however, as they violate generally accepted concepts of the nature of bonding in metal carbonyl derivatives.

Zingales and co-workers have prepared derivatives of $(\phi_2E)_2C_2H_4$

(E = P, As) which, depending on the mode of preparation, are either the usual bidentate derivatives $M(CO)_4D$ and $M(CO)_2D_2$, or the binuclear complexes $L_3M_2(CO)_6$ (*61, 338, 339*). Application of the inert gas formalism to these complexes provides the two alternative structures (19) and (20), both



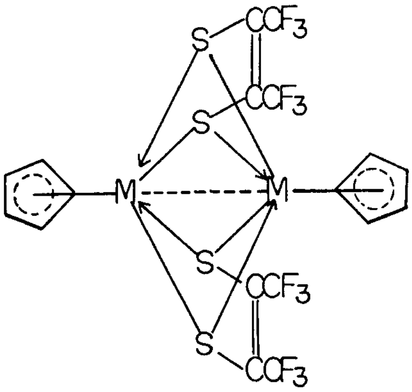
(19)



(20)

analogous to structures reported for mixed carbonyl complexes. Structure (19) is similar to diphosphine derivatives discussed above; structure (20) is analogous to the complex hydroxo-bridged anions reported by Hieber (*162*). The infrared spectra support a *cis* orientation of the carbonyl groups, consistent with either structure. Solubility limitations have unfortunately prevented further studies which might provide evidence in support of one structure or the other.

c. S-Bridged. Several bridged complexes containing sulfur but not CO have been prepared from the metal carbonyls or carbonyl-containing derivatives. The reaction of $[CpMo(CO)_3]_2$ with $(CH_3)_2S_2$ results in the formation of a brown complex whose composition corresponds to $CpMo(CH_3)_2S_2$ and whose diamagnetism supports a dimeric structure containing four S bridges (*184*). The reaction of $(CH_3)_2S_2$ with $[CpCr(CO)_3]_2$ or $[CpCr(CO)_3]_2Hg$ gives the unstable, purple $Cp_2Cr_2(CH_3S)_3$. No magnetic data are available for this derivative, so it cannot be determined whether a metal-metal bond connects the two Cr atoms, or whether possibly one Cr is bonded to an H abstracted from the solvent. A purple-brown complex, whose diamagnetism suggests structure (21), is obtained through the reaction of $[CpM(CO)_3]_2$ (M = Cr, Mo) and bis(trifluoromethyl)dithietene (*184*). $[\pi\text{-}CpM(CO)_2SCH_3]_2$ complexes structurally analogous to phosphine derivatives (structure 11) have also been prepared from $CpMH(CO)_3$ (M = Mo, W) and Me_2S_2 (*323*). The complexity of the infrared spectrum

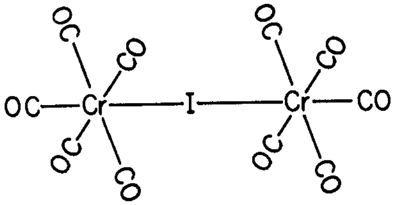


(21)

for the Mo derivative makes it appear that the prepared substance is a mixture of geometrical isomers.

d. Halogen-Bridged. Several binuclear complexes believed to have two bridging halogen groups have been prepared through halogenic oxidation of $M(CO)_4D$ complexes in which D is a bidentate ligand bonding through N (*271*), As (*201*), or S (*213*) (Table VIII). The evidence in support of the proposed structures, however, is by no means unequivocal.

Oxidation of $Cr_2(CO)_{10}^{2-}$ with aqueous I_2—KI solution gives red, paramagnetic $(CO)_5CrICr(CO)_5$ (*34*). Infrared evidence is consistent with a structure in which two octahedra are joined at a point by a single I bridge:



(22)

E. Reaction Mechanism and Kinetics

The mechanism of the displacement of CO from the hexacarbonyl by charge-donating groups has been studied by Strohmeier and co-workers, and by other groups.

Ercoli and co-workers, who studied the gas phase CO exchange reaction with $Cr(C^{14}O)_6$, found the exchange to be first order with respect to CO, and concluded that exchange involved slow fission of Cr—C bonds, followed by rapid recombination (*245*):

$$Cr(CO)_6 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr(CO)_5 + CO \qquad k_2 \gg k_1 \tag{23}$$

Massey and Orgel (*220*) observed that $Cr(CO)_6$, when irradiated in a methyl methacrylate polymer matrix or a KBr disc, turned yellow, and that the color change was accompanied by the formation of new carbonyl stretching bands in the infrared. The absence of potential electron donors in these systems led to the postulation of the $Cr(CO)_5$ species. Similar color changes were noted in irradiated solutions of hexacarbonyls in *n*-hexane (*95*). Sheline and co-workers irradiated hexacarbonyls dissolved in solid methylcyclohexane-isopentane glasses at liquid nitrogen temperatures, and noted the formation of CO stretching bands characteristic of the displacement of one CO from the octahedron to leave a square pyramid of carbonyl groups about the metal (*273, 274*). When the diamagnetic solutions were warmed to the softening temperature of the glass (160°K) the spectrum rapidly changed to one similar to that of $Fe(CO)_5$, in which the CO's are arranged in a trigonal bipyramid (*152*). It was supposed that in the solid glass the CO groups are not free to rearrange to the more favored trigonal bipyramid. $W(CO)_6$ sublimed onto a coldfinger *in vacuo* at liquid nitrogen temperatures becomes yellow-brown upon irradiation (*274*). Upon introduction of acetonitrile into the apparatus after the completion of the irradiation, $W(CO)_5(NCCH_3)$ is immediately formed:

$$W(CO)_5 + NCCH_3 \rightarrow W(CO)_5NCCH_3 \qquad (24)$$

Finally, the exchange of CO in $M(CO)_6$ does not occur in the dark, but occurs rapidly in the presence of ultraviolet radiation (*19, 313*). These results are consistent with the rapid formation of $M(CO)_5D$ after the initial production of $M(CO)_5$.

The quantum yield at 3660 Å for the production of $M(CO)_5D$ is approximately 1, and is independent of the metal (*196, 283, 291, 301*).

The mechanism for the formation of $M(CO)_4D_2$ (*302*) involves the two competing processes (A) and (B):

$$\begin{array}{ll} M(CO)_5D \xrightarrow{h\nu} M(CO)_5D^* \xrightarrow{(A)} M(CO)_4D + CO & \\ \qquad\qquad\qquad\quad \downarrow (B) & (25) \\ \qquad\qquad\quad\;\; M(CO)_5 + D & \end{array}$$

The quantum yields for the formation of $M(CO)_4D_2$ with two different energies of radiation are given in Table IX (*303*). If it is assumed, in analogy to the formation of the mono derivatives, that the quantum yield for reaction (25-A) is approximately 1, the observed quantum yields are a measure of the partition of the overall reaction between relations (25-A) and (25-B). The lower quantum yields at lower energy of radiation are consistent with greater M—CO bond energies than MD bond energies. For other ligands, reaction rates decrease in the order py > THF > Et_3N > ethyl acetate > acetone. This order is essentially independent of the metal

TABLE IX
QUANTUM YIELDS, FORMATION OF $M(CO)_4py_2$

Wavelength (Å)	Quantum yields in benzene for photochemical formation of: $Cr(CO)_4py_2$	$Mo(CO)_4py_2$	$W(CO)_4py_2$
3660	0.21	0.16	0.11
4360	0.13	0.11	0.08

employed (*306*), although quantum yields in Table IX vary, Cr > Mo > W.

The mechanism for the C^{14} exchange in $ArM(CO)_3$ involves displacement of a CO, followed by exchange, in analogy to mechanisms discussed above (*304*).

III. Anionic Derivatives

The anionic derivatives of the Group VIB metal carbonyls may be classified as follows:

(a) Carbonyl metallate ions, $M(CO)_5^{2-}$, $M_2(CO)_{10}^{2-}$, $M_3(CO)_{14}^{2-}$, and possibly higher homologs (*25, 26, 27, 30, 33, 36*) in which the metal atoms are joined by metal-metal bonds. They are produced most readily through the reduction of the hexacarbonyls with $NaBH_4$ or an alkali metal in liquid ammonia. With the exception of the recently reported $W_3(CO)_{14}^{2-}$ (*35*), these ions and their derivatives have been reviewed by Hieber *et al.* (*160*) and will not be further discussed here.

(b) Complex products of the base reactions of the hexacarbonyls (*157, 158, 161, 162, 163, 169*), many of which are polynuclear and contain hydroxo or other bridging groups, e.g., $(OC)_3Cr(OH)_3Cr(CO)_3^{2-}$ (*169*), some of which can be precipitated as the hydrides with strong acids, e.g., $W_4(CO)_{12}(H_2O)_4H_4$ (*166*). These products are also discussed by Hieber *et al.* (*160*).

(c) Mixed complexes of the zerovalent metal carbonyls and anionic substituents, now to be discussed in more detail.

The reaction of *N*-methylpyridinium iodide (*126, 127, 223*) or the halide (Cl^-, Br^-, I^-) (*5, 7*) salt of a quaternary amine with a metal hexacarbonyl yields the corresponding salt of the pentacarbonyl halide, e.g.,

$$Cr(CO)_6 + N\text{-}CH_3NC_5H_5{}^+I^- \xrightarrow[\Delta]{\text{dioxane}} [C_5H_5NCH_3]^+[Cr(CO)_5I]^- + CO \qquad (26)$$

Base reaction products may also be used as routes to their sodium salts (*37*).

Analogous methods have been employed in the preparation of anionic derivatives of SCN^- (*334*) and HCO_3^- (*6*). The yellow, diamagnetic, crystalline halogen derivatives are relatively stable. Infrared spectra are consistent with the expected C_{4v} symmetry of the anions, and the positions of the CO stretching modes are about 100 cm^{-1} lower than for the neutral carbonyl halides of Mn and Re, as is to be expected as a result of the greater negative charge on the metal for the former.

Reaction of $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_4en$ with potassium acetylide salts in liquid ammonia results in the formation of yellow-green to orange salts, $K_3[M(CO)_3(CCR)_3]$ ($R = H$, Me, ϕ) (*230, 231*). CO and CC stretching frequencies indicate that the acetylenic triple bonds do not function as π-acceptors to an appreciable extent. It is likely that the carbonyl groups in these anions are mutually *cis*.

Additional routes (*29, 35*) to the preparation of anionic CN^- derivatives (*32, 33*) $M(CO)_{6-x}(CN)_x^{-x}$ ($x = 1$–3) have also been reported.

Reaction of $W(CO)_6$ and $Li\phi$ yields anions which can be precipitated as the Me_4N^+ salts (*122*). Orange $Me_4N^+W(CO)_5CO\phi^-$ (m. 102.5°) and yellow $Me_4N^+W(CO)_5COMe^-$ (m. 143°) can be methylated with diazomethane to give neutral complexes, orange, diamagnetic $W(CO)_5CO\phi(Me)$, and yellow, diamagnetic $W(CO)_5CO(Me)(Me)$, which has been formulated on the basis of infrared and NMR evidence as (methoxymethylcarbene)$W(CO)_5$.

IV. π-Bonded Derivatives

A. π-ARENE DERIVATIVES

π-Arene derivatives of the Group VIB metal carbonyls have been included among the topics of a number of review articles (*108, 109, 330, 337*), and material reviewed there will not be repeated. The reader's attention is called especially to a review by Fischer and Fritz (*109*). This section deals, therefore, only with the chemistry of π-arene complexes reported from 1961 to date.

1. *Preparation and Physical Properties*

Table X gives a compilation of arene derivatives not reported in earlier reviews. Literature before 1961 dealing with the preparation of various derivatives is also quite extensive (*86, 99, 100, 103, 118, 124, 128, 129, 179, 224, 232, 233, 238, 239, 256*).

Strohmeier has found that the most suitable temperature for the direct preparation of arene metal tricarbonyls is just below the decomposition temperature of the complex (*279*). The thermal stability of the complexes is related to the donor strength of the π-aromatic system, and thus the preparation of the derivatives is facilitated by the presence of charge-

TABLE X
π-ARENE DERIVATIVES OF GROUP VIB METAL CARBONYLS

Complex	Color	M.P. (°C)	Physical measurements[a]	Ref.
(Me$_3$Siϕ)Cr(CO)$_3$	Yellow	72–73	3	(*269*)
(Me$_3$Geϕ)Cr(CO)$_3$	Yellow	79–79.5	3	(*269*)
(Me$_3$Snϕ)Cr(CO)$_3$	Yellow	78.5–79	3	(*269*)
(CH$_2\phi_2$)Cr(CO)$_3$	Yellow	98–99	3	(*237*)
(C$_2$H$_2\phi_2$)Cr(CO)$_3$	Yellow	130–131.5	3	(*237*)
(Dihydrotetracene)Cr(CO)$_3$	Yellow	184.5–185.5	3	(*237*)
(Diphenylfulvene)Cr(CO)$_3$	Dark brown	203–209 dec	3	(*135*)
(*o*-MeC$_6$H$_4$COCH$_3$)Cr(CO)$_3$	Red	65–66	—	(*155*)
(*p*-MeC$_6$H$_4$COCH$_3$)Cr(CO)$_3$	Red	107	—	(*155*)
(*p*-F$_2$C$_6$H$_4$)Cr(CO)$_3$	Yellow	111	—	(*281*)
(*p*-Cl$_2$C$_6$H$_4$)Cr(CO)$_3$	Yellow	88	—	(*281*)
(*m*-MeOC$_6$H$_4$COOH)Cr(CO)$_3$	Red	147–148 dec	4, 11	(*212*)
(Meϕ)Mo(CO)$_3$	Yellow	127–128	—	(*279*)
(Fϕ)Mo(CO)$_3$	Yellow	—	—	(*279*)
(*p*-Me$_2$C$_6$H$_4$)Mo(CO)$_3$	Yellow	139–140	—	(*279*)
(Meϕ)W(CO)$_3$	Yellow	140–142	—	(*280*)
(*p*-Me$_2$C$_6$H$_4$)W(CO)$_3$	Yellow	143–145	—	(*280*)
(Biphenylene)Mo(CO)$_3$	Orange	163–185 dec	3	(*63*)
(μ-Biphenylene)[Mo(CO)$_3$]$_2$	Scarlet	204	3, 8	(*63*)
1-[(Benzyl)Cr(CO)$_3$]ferrocene	—	164.5	4	(*57*)
1[(Phenyl)Cr(CO)$_3$]-4-phenylbutadiene	Orange-red	150–152	4	(*58, 222*)
1,4[(Phenyl)Cr(CO)$_3$]$_2$-butadiene	—	186–188 dec	4	(*58, 222*)
1,4[(Phenyl)Cr(CO)$_3$]$_2$-butadiene[Fe(CO)$_3$]	—	193–195 dec	4	(*58, 222*)
1-[(Phenyl)Cr(CO)$_3$]-4-phenylbutadiene[Fe(CO)$_3$]	—	193–195 dec	4	(*222*)
(Benzoylacetone)Cr(CO)$_3$	Red	115–117	3	(*60*)
(3-Methyl-5-phenylpyrazole)Cr(CO)$_3$	Yellow	165–167 dec	3	(*60*)
(3-Methyl-5-phenylisoazole)Cr(CO)$_3$	Orange-brown	115–116.5 dec	3	(*60*)
(Mesitylene)Cr(CO)$_2$(py)	Red	—	3, 6	(*295, 298*)
(Mesitylene)Cr(CO)$_2$(DMSO)	Orange	150	3, 6	(*295, 298*)
(Mesitylene)Cr(CO)$_2$(ethylene)	Red	—	3	(*119*)
(tere)Cr(CO)$_2$(NCϕ)	Brown-red	121	—	(*296*)
(tere)Cr(CO)$_2$(NCMe)	Dark violet	—	—	(*296*)
(tere)Cr(CO)$_2$(quin)	Blue-black	166 dec	—	(*296*)
(tere)Cr(CO)$_2$(aniline)	Brown	90 dec	—	(*296*)
(tere)Cr(CO)$_2$(Pϕ_3)	Red	160	3, 6	(*295, 298*)
(tere)Cr(CO)$_2$(py)	Violet	147	3, 6	(*295, 298*)
(tere)Cr(CO)$_2$(pip)	Violet	140	3, 6	(*295, 298*)
(Benzene)Cr(CO)$_2$(py)	Red	—	3, 6	(*295, 298*)
(Benzene)Cr(CO)$_2$(DMSO)	Yellow	133	3, 6	(*295, 298*)

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[a] See key to symbols (Table IV).

donating substituents on the ring. It is especially to be noted that Mo and W derivatives have been prepared under these conditions (*278, 279, 280*).

2. Structures and Bonding

X-ray data on (benzene)$Cr(CO)_3$ (*11, 73, 74*) and (biphenyl)$[Cr(CO)_3]_2$ (*12, 75*) have been reported. A detailed x-ray investigation of (benzene)$Cr(CO)_3$ (*11*) shows the molecule to possess C_{3v} symmetry, with the C_3 axis joining the centers of gravity of the benzene ring and the three oxygens, passing through the Cr atom. The Cr—C—O bonds are linear. The data support a "fixed Kekule" structure for benzene in the complex, and suggest that the d^2sp^3 hybridization in $Cr(CO)_6$ is maintained in the benzene derivative. A recent crystallographic study of (hexamethylbenzene)$Cr(CO)_3$ also supports d^2sp^3 hybridization on Cr, in that the $Cr(CO)_3$ moiety is oriented in a way such that the other three presumably octahedral Cr orbitals are directed toward the midpoints of the alternate C—C bonds of the aromatic ring (*15*). (Biphenyl)$[Cr(CO)_3]_2$ has a structure similar to that of (benzene)$Cr(CO)_3$, with the Cr atoms on *trans* sites (*12*).

The isomeric distribution obtained through the acetylation of (toluene)$Cr(CO)_3$ has been compared to that obtained for free toluene, and the result [(methylacetophenone)$Cr(CO)_3$: *ortho,* 39%; *meta,* 15%; *para,* 46%; methylacetophenone: *ortho,* 9.3%; *meta,* 1.45%; *para,* 89.3%], with the evident decrease in the *ortho-para* directing ability in the carbonyl derivative, again is consistent with a "fixed Kekule" structure in arene metal carbonyls (*155*). It has been proposed that a partial annihilation of the delocalization of charge in the carbonyl derivative diminishes the distribution of the inductive effect to the *para* position, and thus also increases the *ortho* directing ability.

3. Molecular Spectroscopy

a. Infrared Spectra. Under the "local symmetry" of the carbonyl groups (Section II,C), arene metal tricarbonyls belong to the C_{3v} point group. Band position and intensity arguments lead to the assignment of the two infrared-active CO stretching modes ($A_1 + E$) as the weaker, higher energy band, and the stronger, low energy band, respectively (*244*). The positions of the bands with respect to those for the structurally similar (dien)$Cr(CO)_3$ are indicative of extensive π-accepting ability on the part of the ring (*141*). In KBr, band broadening or splitting attributable to crystal effects has been observed for many derivatives, but splitting in solution has also been observed for complexes in which all orbitals of the p_π sextet are not equivalent, e.g., for heterocyclic systems and seven- or eight-membered trienes, formally conjugated, but in which conjugation is interrupted by intervening methylene groups (*141*).

It has been observed experimentally (*141*) and verified by a theoretical calculation (*54*) that charge-releasing ring substituents transfer more charge to the metal than do charge-withdrawing groups, and thus derivatives of the former exhibit the lower CO stretching frequencies. This effect is illustrated in Table XI.

TABLE XI
VARIATION OF ν_{CO} WITH RING SUBSTITUENT FOR ARENE CHROMIUM TRICARBONYL DERIVATIVES

Ring substituent, X	ν_{CO} for $XArCr(CO)_3$ (hexane)	Ref.	Hammett σ_{para}
Cl	1992, 1930, 1926	(*54*)	+0.227
F	1996, 1930, 1927	(*141*)	+0.062
H	1987, 1917	(*141*)	0.000
CH_3	1983, 1914	(*141*)	−0.170
NH_2	1977, 1906	(*141*)	−0.660
$N(CH_3)_2$	1969, 1897	(*54*)	−0.830

A strong δMCO triplet, ca. 500–700 cm^{-1}, has been observed for a variety of arene derivatives (*10*) and is diagnostic of symmetrical trisubstitution products. A typical spectrum in the KBr region of the infrared, that of (p-xylene)$Cr(CO)_3$, is shown in Fig. 15 (*178*). The two bands at lower frequencies are those expected for M—C stretching modes.

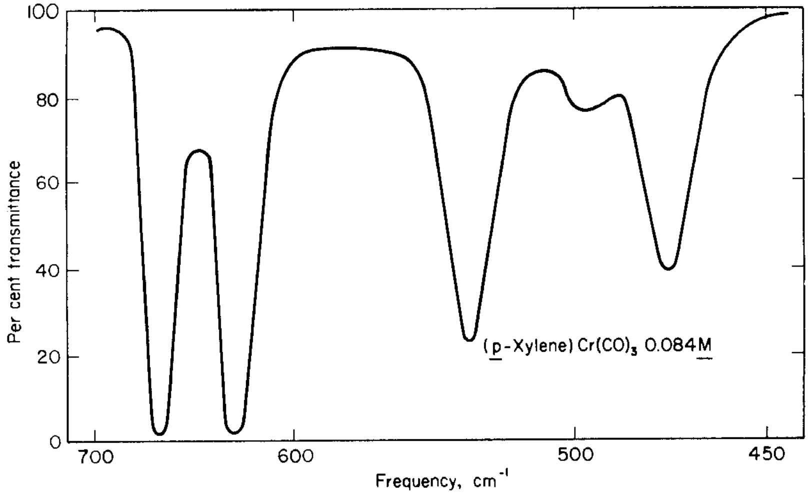


FIG. 15. Infrared spectrum (700–450 cm^{-1}) of (p-xylene)$Cr(CO)_3$ [from Humphrey (*178*)].

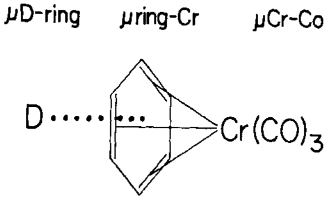
For (benzene)$Cr(CO)_3$, the fifteen expected infrared-active normal modes for a molecule of C_{3v} symmetry have all been observed. The deviations of ring frequencies from those of free benzene are not large, and are smaller than deviations observed for dibenzenechromium. This effect has been attributed to weaker π-bonding in the carbonyl complex (*145*, *146*, *178*).

b. Ultraviolet and Visible Spectra. The ultraviolet spectra of aromatic metal tricarbonyls (*59*, *101*, *336*) have been reviewed by Fischer and Fritz (*109*). The spectra consist of three absorptions, ca. 320, 260, and 220 mμ, log ε ~3.50, 4.05, and 4.80, respectively. The band ca. 260 mμ is diagnostic of a metal carbonyl moiety regardless of the nature of the π-bonded organic portion of the molecule, be it arene, cyclopentadienyl, or conjugated diene (*205*). There is no regular pattern of band shifts with the varying electronic nature of the arene substituent groups (*141*).

4. Dipole Moments

Early dipole moment work (*134*, *255*, *300*) has been reviewed by Fischer and Fritz (*109*).

It has been noted that dipole moments for arene derivatives increase with the increasing electron-releasing ability of ring substituents, supporting polarization of the Ar—M bond in the direction of the metal (*134*, *255*). Solvents which can function as charge donors, e.g., dioxane, can increase the dipole moments for arene metal tricarbonyls over their values in nonpolar solvents (*294*, *300*). The results have been interpreted in terms of the ability of the bonded arene group to function as a charge acceptor:



(27)

Solvent shift studies on arene metal tricarbonyl derivatives support polarization of M—CO bonds in the direction of the metal (Section II,A) (*54*).

5. Other Physical Measurements

Fischer and Fritz (*109*) have reviewed work on dissociation constants (*129*, *239*), microwave spectra (*324*), the Szilard-Chalmers process (*21*), and vapor pressure measurements (*72*), for all of which no new work has been reported.

6. *Some Individual Derivatives*

a. (m-Methoxybenzoic Acid)Cr(CO)$_3$. Ortho and *meta* disubstituted arenes containing two different substituent groups are asymmetric with respect to the center of the ring, and thus their π-metal carbonyl derivatives should exhibit optical activity. The first resolution of a Group VIB metal arene complex has been reported by Cais and co-workers (*212*), who have separated the diastereoisomers of (*m*-methoxybenzoic acid)Cr(CO)$_3$ as the brucine salts.

b. Derivatives of Biphenylene and Diphenyl Fulvene. Biphenylene and diphenyl fulvene carbonyl derivatives π-bonded through the six-membered rings have been prepared (*63, 135*). X-ray results indicate that μ-biphenylenebis(tricarbonylmolybdenum) is centrosymmetric and, therefore, that the Mo(CO)$_3$ groups are *trans*. Independent use of the six-membered rings supports a Kekule structure having no unsaturation of the four-membered ring. The results for 6,6-diphenylfulvene are interesting in that the Cr π-complex is bonded through the six-membered ring, while the Fe derivative is bonded through the five-membered ring; in both instances the metal-carbonyl moiety contains three CO groups (*135*)

7. *Kinetics and Mechanism*

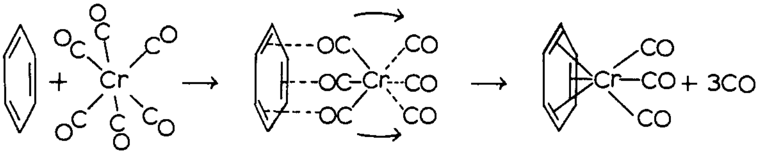
It was originally proposed that the formation of arene metal tricarbonyls involved the equilibrium

$$M(CO)_6 + Ar \rightleftharpoons ArM(CO)_3 + 3CO \qquad (28)$$

and that the typical equilibrium expression

$$K = \frac{[M(CO)_6][Ar]}{[ArM(CO)_3][CO]^3} \qquad (29)$$

described the behavior of the system (*128, 129, 232, 233, 239*). An S$_N$2 "Walden Inversion"-type mechanism, with expulsion of the three carbonyls on the side of the metal opposite the approaching arene, followed by inversion of the three remaining carbonyls has been proposed (*129*):



(30)

Although this mechanism has been questioned (*308*), it is consistent with recent kinetic data which show the reaction to be first order in Cr(CO)$_6$ for mesitylene and benzene (*53a*).

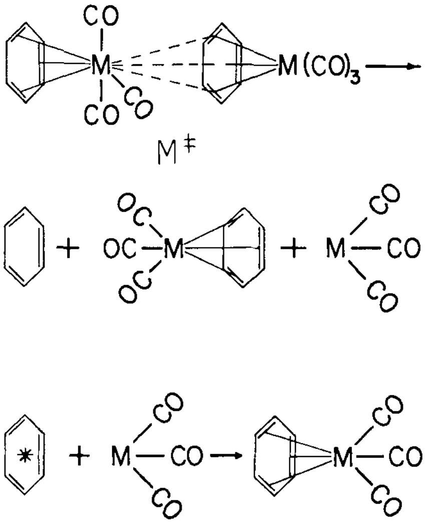
Exchange reactions have been extensively studied. The exchange

$$ArM(CO)_3 + Ar^* \rightarrow Ar^*M(CO)_3 + Ar \qquad (31)$$

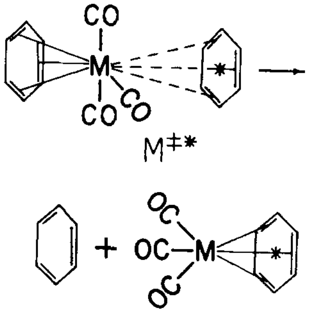
has been shown to follow the rate expression

$$k = k_{11}[ArM(CO)_3]^2 + k'_{11}[ArM(CO)_3][Ar] \qquad (32)$$

where $k_{11} > k'_{11}$ (*311, 314*). The rate is believed to be determined by two distinct processes (33, 34):



(33)



(34)

For each process the rate-determining step is the formation of the transition state (M‡ or M‡*). Dipole measurements (*294*) indicate that the bound aromatic group in arene metal carbonyls can function as a charge acceptor; for the two processes the *d* metallic orbitals of $ArM(CO)_3$ and the π orbitals of the free aromatic group function as charge donors. Since k_{11} is greater than k'_{11}, the former are the stronger charge donors. Charge-releasing substituents on the ring increase the respective rate constants; linear relationships are obtained from plots of log k_{11} and log k'_{11} against the Hammett σ *para* substitution constants (*314*). Exchange rates vary, Cr < W < Mo. Rates of exchange also increase with increased dielectric constant of the solvent employed as the reaction medium. This effect has been attributed to an increase in k_{II} brought about by solvation of the bound ring in (benzene)$Cr(CO)_3$; the steric factor governing the collision of two such molecules to give the activated complex is thus decreased (*317*).

The rates of exchange for arene and quasiarene tricarbonyl systems increase in the order, benzene $\ll$ cycloheptatriene $<$ naphthalene (*310, 314*). The faster exchange of activity for (cycloheptatriene)$Cr(CO)_3$ stems from the greater ease with which the complex dissociates, as is indicated by the thermal instability of the complex, and by the ease with which the cycloheptatriene group may be displaced by electron-donating ligands to yield the *cis* complexes $M(CO)_3D_3$ (Section II,D). The velocity of the reaction obeys the expression

$$k = k_{\text{I}}[C_7H_8Cr(CO)_3] + k_{\text{II}}[C_7H_8Cr(CO)_3][C_7H_8] \ (\mathit{312}) \qquad (35)$$

8. Complex of the Type, $M(CO)_5(Ar)$

Infrared evidence supports the existence of a new type of π-complex, $M(CO)_5(Ar)$, prepared through ultraviolet irradiation at low temperature of the hexacarbonyl and a wide variety of arenes, and polycyclic and heterocyclic aromatic systems (*276a*). Although previously reported complexes of benzene as a monodentate ligand have involved "edge-on" bonding of the ring to a single center of unsaturation (*260a*), spectral evidence here supports bonding to the ring center, while involving only two ring electrons. A bonding scheme postulates overlap of the filled A_{2u} orbital on benzene with the vacant $d_z{}^2$ metallic orbital, and back donation from the filled d_{xz} metallic orbital to the B_{1g} ring orbital; back bonding might also involve δ bonding from the metallic d_{xy} metal orbital to the E_{2u} ring orbital.

B. π-CYCLOPENTADIENYL AND RELATED DERIVATIVES

1. Introduction

Early work on π-cyclopentadienyl transition metal derivatives and their Group VIB metal carbonyl complexes has been reviewed by Wilkinson and Cotton (*330*), Fischer (*102*), and Fischer and Fritz (*108*). Ionic π—Cp derivatives have recently been reviewed by King (*185b*). The first of these reviews is particularly recommended for a discussion of bonding in these complexes. Material reviewed in the first three of these sources will not be repeated here; the present review discusses work reported since 1960.

The cyclopentadienyl and related π-bonding groups (e.g., cycloheptatrienyl) supply an odd number of electrons to the transition metal atom. Nonetheless, their Group VIB carbonyl derivatives obey the inert gas formalism, and thus for nonionic derivatives an odd electron must be supplied to the metal. Table XII gives pertinent data for cyclopentadienyl

TABLE XII
CYCLOPENTADIENYL AND RELATED DERIVATIVES

R	R′	M	Color	M.P. (°C)	Physical measurements[a]	Ref.
(A) $RCpMR'(CO)_3$ derivatives						
H	CN	W	Orange	—	3, 10	(*71a*)
H	$(CF_3)_2As$	Mo	Yellow-orange	111–117	3, 7	(*87*)
H	$OCOCF_3$	Mo	Red	83.5–84.5	3, 4	(*90*)
H	$OCOCF_3$	W	Red	90.5–91.5	3, 4	(*90*)
H	$OCCF_3$	Mo	Yellow	64–65	3, 4, 7	(*190*)
H	OCC_3F_7	Mo	Yellow	46–47	3, 4, 7	(*190*)
H	CF_3	Mo	Yellow	153	3, 4, 7	(*190*)
H	C_3F_7	Mo	Yellow	81–83	3, 4, 7	(*181a, 190*)
H	$OCCF_3$	W	Yellow	80–82	3, 4, 7	(*190*)
H	OCC_3F_7	W	Yellow	53–55	3, 4, 7	(*190*)
H	CF_2CF_2H	Mo	Yellow-orange	53–54	3, 7	(*195, 323*)
H	OCEt	Mo	Red	—	7	(*208*)
H	OCEt	W	Orange	ca. 5	3, 7	(*208*)
H	CF_2CF_2H	W	Yellow	65–65.5 dec	3, 7	(*323*)
H	$CH_2{=}CHCH_2$	Mo	Yellow	~ -5	3, 7	(*84*)
H	$CH_2{=}CHCH_2$	W	Yellow	24–26	3, 7	(*150*)
H	Me_2CH	W	Dark yellow	Oil	3, 7	(*150*)
H	CH_3SCH_2	Mo	—	66–67	3, 7	(*188*)
i-Pr	I	Mo	—	92–94	3	(*9*)
CHMeEt	I	Mo	—	75	3	(*9*)
$CHEt_2$	I	Mo	—	45	3	(*9*)
$CH\phi Me$	I	Mo	—	76	3	(*9*)
p-$MeOC_6H_4CH_2$	I	Mo	—	78	3	(*9*)
CHMe-*i*-Pr	I	Mo	—	Oil	3	(*9*)
i-Pr	Me	Mo	—	~ -25	3	(*9*)
i-Pr	Et	Mo	—	~ -15	3	(*9*)
$CHEt_2$	Me	Mo	—	Oil	3	(*9*)
$CHEt_2$	Et	Mo	—	Oil	3	(*9*)
$CH\phi Me$	Me	Mo	—	Oil	3	(*9*)
H	$SnCl_3$	Mo	Yellow	187	3	(*47a*)
H	$SnCl_3$	W	Yellow	164 dec	3	(*47a*)

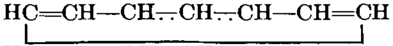
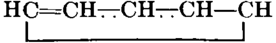
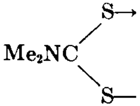
H	$Sn\phi_3$	Mo	—	212.5–213.5	3	(*235*)
H	$Sn\phi_3$	W	—	229–230.5	3	(*235*)
H	$Pb\phi_3$	W	—	210–211.5	3	(*235*)
H	$Pb\phi_3$	Mo	—	205	3	(*235*)
H	$Sn\phi_3$	Cr	—	220–222	3	(*235*)
H	$Sn\phi Cl_2$	Mo	—	109–110	3	(*235*)
H	$Sn\phi Cl_2$	W	—	112–114	3	(*235*)
n-Pr	[dimer]	Mo	Red	200 dec	3	(*9*)
i-Pr	[dimer]	Mo	Red	163	3, 4	(*9*)
CHMeEt	[dimer]	Mo	Red	170	3, 4	(*9*)
$CHEt_2$	[dimer]	Mo	Red	152	3, 4	(*9*)
CHMe-*n*-Pr	[dimer]	Mo	Red	117–119	3, 4	(*9*)
$CH\phi Me$	[dimer]	Mo	Dark red	125 dec	3, 4	(*9*)
$CH\phi_2$	[dimer]	Mo	Brown	203–250	3, 4	(*9*)
p-$MeOC_6H_4CH_2$	[dimer]	Mo	Brown	103 dec	3, 4	(*9*)
Cyclohexyl	[dimer]	Mo	Red	180	3, 4	(*9*)
i-Pr	[dimer]	W	Red	195	3, 4	(*9*)
$CHEt_2$	[dimer]	W	Red	184	3, 4	(*9*)
H	$CpW(CO)_3$	Mo	Red	—	4	(*9*)
H	$CpFe(CO)_2$	Mo	Red-violet	200	3	(*150*)
(B) $RCpM\colon R'(CO)_2$ derivatives						
H	 $HC{=}CH{-}CH{\cdots}CH{\cdots}CH{-}CH{=}CH$	Mo	Orange	111–112	3, 4, 7	(*185a, 186*)
H	 $HC{=}CH{\cdots}CH{\cdots}CH{-}CH$	Cr	Yellow	73–74	3, 5, 6, 7	(*136*)
H	$H_3C{-}CH{\cdots}CH{\cdots}CH_2$	Cr	Yellow	74–75	3, 7	(*137, 144*)
H	$H_2C{\cdots}CH{\cdots}CH_2$	Mo	Lemon yellow	134 dec	3, 7	(*84*)
H	$H_2C{\cdots}CH{\cdots}CH_2$	W	Yellow	—	3, 7	(*150*)
H		Mo	Purple	191 dec	3	(*79*)
H	$I\cdot;\ \phi NC\rightarrow$	Mo	Red	75	3	(*181*)
H	$H_2C{=}SCH_3$	Mo	Yellow	66–67	3, 5, 7, 10	(*188*)
H	$CH_3OC_6H_4N{=}N{-}$	Mo	Orange-red	78–79	3, 5, 7	(*189*)
CH_3CO	NO	Cr	Red	27–28	3	(*133*)

TABLE XII (*Continued*)

$\overset{-}{Cp}$	M	Color	M.P.	Physical measurements	Ref.
(C) $\overset{-}{Cp}M(CO)_3$ derivatives					
$\phi_3\overset{+}{P}\overset{-}{Cp}$	Mo	Yellow	—	3, 7	*(8)*
$Me_2\overset{+}{N}CH\overset{-}{Cp}$	Cr	Red-violet	218–222 dec	3, 4, 7	*(187)*
$Me_2\overset{+}{N}CH\overset{-}{Cp}$	Mo	Red	230–240 dec	3, 4, 7	*(187)*
$(Me_2\overset{+}{N})_2C\overset{-}{Cp}$	Cr	Red	241–243 dec	3, 4, 7	*(187)*
$(Me_2\overset{+}{N})_2C\overset{-}{Cp}$	Mo	Yellow	281–284 dec	3, 4, 7	*(187)*

Complex[b]	Color	M.P.	Physical measurements[a]	Ref.
(D) Ionic derivatives				
$CpCr(CO)_4{}^+B^-$	Yellow	—	3, 5	*(138)*
$CpMo(CO)_4{}^+P^-$	—	195 dec	3	*(107)*
$CpW(CO)_4{}^+P^-$	—	260 dec	3	*(107)*
$CpMoNH_3(CO)_3{}^+R^-$	Bright red	—	3, 7	*(123)*
$CpMoNH_3(CO)_3{}^+T^-$	Orange-yellow	—	3, 7	*(123)*
$CpMoN_2H_4(CO)_3{}^+R^-$	Dark red	—	3, 7	*(123)*
$CpMoN_2H_4(CO)_3{}^+T^-$	Orange-red	—	3, 7	*(123)*
$CpWNH_3(CO)_3{}^+R^-$	Orange	—	3, 7	*(123)*
$CpWNH_3(CO)_3{}^+T^-$	Yellow	—	3, 7	*(123)*
$CpWN_2H_4(CO)_3{}^+R^-$	Orange	—	3, 7	*(123)*
$CpWNH_2(CO)_3{}^+T^-$	Yellow-orange	—	3, 7	*(123)*
$CpMo\text{-}\pi\text{-}MeCH{=}CH_2{}^+P^-$	Yellow	—	3, 7	*(123)*
$CpW\text{-}\pi\text{-}MeCH{=}CH_2(CO)_3{}^+P^-$	Yellow	—	3, 7	*(150)*
$CpMo\text{-}\pi\text{-}CH_2DCH{=}CH_2(CO)_3{}^+P^-$	Yellow	—	3, 7	*(84)*
$CpMo\text{-}\pi\text{-}CH_2{=}CH_2(CO)_3{}^+P^-$	Yellow	104 dec	3, 7	*(84, 106)*
$CpW\text{-}\pi\text{-}CH_2{=}CH_2(CO)_3{}^+A^-$	—	120	3	*(106)*

$CpCr(NO)_2CO^+A^-$	Olive brown	143 dec	3, 5	(*120*)
$CpWCNCH_3(CO)_3{}^+I^-$	Yellow	153.0–153.2	3	(*71a*)
$CpMo(CNCH_3)_2(CO)_2{}^+I^-$	Yellow	—	3	(*71a*)
$K^+CpMo(CN)_2(CO)_2{}^-$	Yellow	—	3	(*71a*)
$K^+CpW(CN)_2(CO)_2{}^-$	—	—	3	(*71a*)
$[CpW(CO)_3]_2H^+P^-$	Yellow	180–182	7	(*90*)
(E) Other derivatives				
$C_7H_7Mo(CO)_2I$	—	—	—	(*41a*)
$C_7H_7Mo(CO)_2Mn(CO)_5$	Green	—	3	(*186*)
$[(Indenyl)Mo(CO)_3]_2$	Brown	195–197 dec	3	(*192*)
$CpMo(CN\phi)_3Cl$	Red	180 dec	3	(*181*)

[a] See key to symbols (Table IV).
[b] B^- = $BF_4{}^-$; P^- = $PF_6{}^-$; R^- = reineckate; T^- = $B\phi_4{}^-$; and A^- = $AlCl_4{}^-$.

and related derivatives. Section A lists those tricarbonyl derivatives in which the rare gas configuration is satisfied through formation of a single covalent or metal-metal bond. Section B lists dicarbonyl derivatives of groups donating three electrons. A number of cyclopentadienylide tricarbonyl derivatives, in which $[Cp]^-$ donates a sextet of electrons to the metal, are listed in Section C; cationic derivatives of coordinately bonded substituents are listed in Section D; and Section E lists derivatives falling into none of these classes. Polymeric products containing bridging ligands have been discussed in Section II,D, and their characteristics given in Table VIII. Acetylenic derivatives are discussed in Section F (below).

2. Preparation of Derivatives

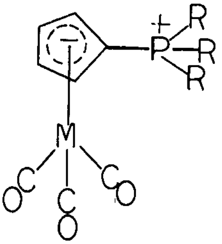
"Simple" derivatives $CpMR(CO)_3$ are typically prepared through reaction of the metal cyclopentadienylide sodium salt or the cyclopentadienyl dimer with a halide (*9, 84, 87, 150, 188, 189, 194*):

$$\begin{matrix} Na^+CpM(CO)_3^- \\ (CO)_3CpM{-}MCp(CO)_3 \end{matrix} + RX \rightarrow CpMR(CO)_3 \qquad (36)$$

Other methods have employed the hydride, $CpMH(CO)_3$ (*107, 138, 195, 323*), or halide, $CpMX(CO)_3$ (*9, 71a*), as starting material. Derivatives substituted on the cyclopentadienyl ring have been prepared through reaction of fulvenes with the hexacarbonyl (*9*), or through Friedel-Crafts acylation of the ring (*133*). Similar methods are used in the preparation of other types of cyclopentadienyl derivatives; individual reactions will now be discussed in greater detail.

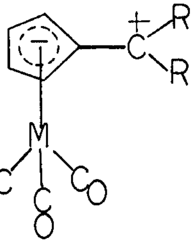
3. Reactions of Cyclopentadienyl and Related Derivatives

Wilkinson and associates (*8*) prepared a derivative of triphenylphosphonium cyclopentadienylide which may be formulated as a zwitterionic species:



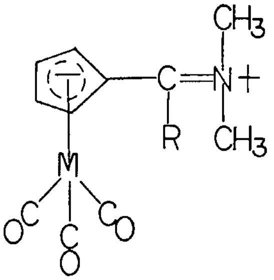
(37)

in which the cyclopentadienylide group is π-bonded to the carbonyl moiety through a sextet of electrons. This result, together with the preparation of dimeric cyclopentadienyl species from substituted fulvenes (*9*), led King and Bisnette (*187*) to propose that the latter reactions proceed through a carbonium ion intermediate:



(38)

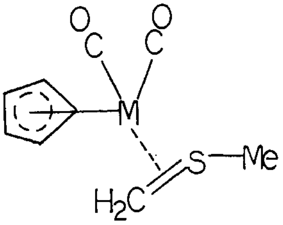
which then abstracts hydrogen from the solvent; dimerization follows. To support this hypothesis, a series of derivatives of dimethylaminofulvenes (Table XII,C), in which the positive charge on carbon can be delocalized and the intermediate thus stabilized:



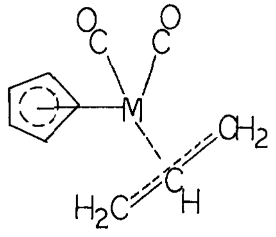
(39)

has been prepared.

Exposure of σ-allyl or σ-H_2CSCH_3 cyclopentadienyl metal tricarbonyls to an ultraviolet source has led to the expulsion of a carbonyl group with the formation of derivatives which may be formulated as complexes in which the erstwhile σ-donating groups now each donate three electrons (*84*, *133*, *188*):

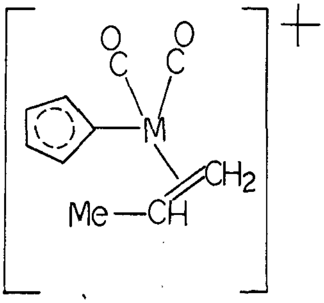


(40a)



(40b)

Bonding in structures (40a) and (40b) may be considered to be related as are bonding in (benzene)M(CO)$_3$ (Section IV,A) and (thiophene)M(CO)$_3$ (Section IV,D). Treatment of the σ-allyl derivative, CpMCH$_2$CH$_2$CH$_3$(CO)$_3$, with H$^+$ yields the cationic π-bonded derivative:



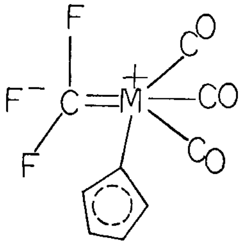
(41)

which may be precipitated as the hexafluorophosphate (*90*). Reduction of this complex with LiBH$_4$ yields CpMCH(CH$_3$)$_2$(CO)$_3$.

Several dicarbonyl complexes, which may best be formulated as involving the donation of three delocalized electrons from the crotyl (*137*, *144*), cycloheptatrienyl (*185a*, *186*), or cyclopentenyl (*136*) groups, have been reported, as have nitrosyl (*120*, *133*) and a formally analogous *p*-anisyldiazonium derivative (*189*).

A number of binuclear derivatives in which Mo is bonded to W (*9*), Sn (*47a*, *235*), Pb (*235*), Fe (*194*), or Mn (*186*) have also been reported (Table XII,A,E).

Acyl derivatives containing the RCO group bonded to the metal have been extensively investigated. The perfluoro derivatives, prepared through reaction of the sodium cyclopentadienylide salt with the perfluoroacyl halide, are the more stable (*190*). These derivatives may be thermally decarbonylated to give the corresponding alkyl derivatives (*190*, *208*); the two types of R group may be distinguished by the position of their proton or fluorine resonances (*190*, *208*). Tracer studies on the decarbonylation of analogous Mn derivatives have shown that the expelled group is a carbonyl rather than an acetyl CO (*71b*). ν_{C-F} values for the alkyl derivatives are significantly lower than for the corresponding acyl complexes, which has led King and Bisnette to postulate a significant "no-bond" resonance contribution:



(42)

in the former (*190*). This hypothesis is supported by the known resistance of the M—C bond to cleavage, and the corresponding susceptibility of F to removal by basic reagents (*190*). The preparation of acyl derivatives through the insertion of CO under pressure has led to the formation, in addition to the expected products, of dimeric products in which the ethyl group has migrated from the metal to the ring (*208*). The recovery of appreciable quantities of butane has led to the postulation that, in the melt, homolysis of the ethyl-metal bond occurs rather easily, and that the ethyl radical formed can either dimerize to butane, or attack the cyclopentadienyl ring to form H and π-$C_2H_5C_5H_4Mo(CO)_3$; the latter radical then dimerizes.

The basic properties of cyclopentadienyl derivatives have been studied by NMR techniques (*91*, *92*). In H_2SO_4 the formation of hydrogenated cyclopentadienyl metal carbonyl cations can be followed by the appearance of a very high field proton resonance (τ = 30–40) characteristic of a metal-hydrogen bond. NMR evidence favors a rapid intramolecular exchange of the proton between the two metal atoms in the cyclopentadienyl carbonyl dimer.

C. DERIVATIVES OF CONDENSED AROMATIC SYSTEMS

The Group VIB carbonyl derivatives of azulene, indene, fluorene, and related compounds have recently been reviewed by Bennett (*39*). In azulene and related compounds, bonding is to both rings, with a metal-metal bond between the two $Mo(CO)_3$ moieties a possible explanation of the diamagnetism of the compounds (*55*, *56*). Evidence indicates that indene and fluorene are bonded through the six-membered ring only (*117*).

Highly colored tricarbonyl derivatives of condensed six-membered ring systems have been prepared through direct reaction of the carbonyl with the ligand (*118*, *129*, *192*). These, together with their properties, are

TABLE XIII
MIXED CARBONYL DERIVATIVES OF CONDENSED AROMATICS

Complex	Color	M.P. (°C)	Physical measurements[a]	Ref.
(Phenanthrene)Cr(CO)$_3$	Red	157–160	3, 4, 5, 6, 8	(*93, 118, 141, 192*)
(Anthracene)Cr(CO)$_3$	Nearly black	189–192 dec	3, 4, 6, 7	(*118, 141, 331*)
(Chrysene)Cr(CO)$_3$	Dark red	129–130 dec	3	(*118, 141*)
(9,10-Dihydroanthracene)Cr(CO)$_3$	Yellow	143–144	3	(*118*)
(Naphthalene)Cr(CO)$_3$	Yellow	150–160 dec	3	(*118, 129, 141*)
(Pyrene) Cr(CO)$_3$	Red	—	—	(*192*)
(Thianaphthene)Cr(CO)$_3$	Yellow	115	3	(*192*)
(Acenaphthacene)Cr(CO)$_3$	Purple-black	175 dec	3, 4	(*192*)

[a] See key to symbols (Table IV).

listed in Table XIII. In addition, several derivatives of substituted naphthalenes, prepared for use in NMR studies, have indicated that bonding of the Cr in these π-complexes is to the "most benzenoid" ring, the one with the greatest electron density (*104*). Thus bonding, for example in (anthracene)Cr$(CO)_3$, would be expected to either of the two equivalent end rings. This hypothesis has been supported by recent NMR studies of the compound: a proton resonance triplet of relative intensities 2:2:4 would be anticipated for bonding to the center ring, whereas the observed 2:2:2:2:2 quintet is expected for end ring bonding (*331*). A recent X-ray investigation of (phenanthrene)Cr$(CO)_3$ also has confirmed end ring bonding (Fig. 16) (*93*).

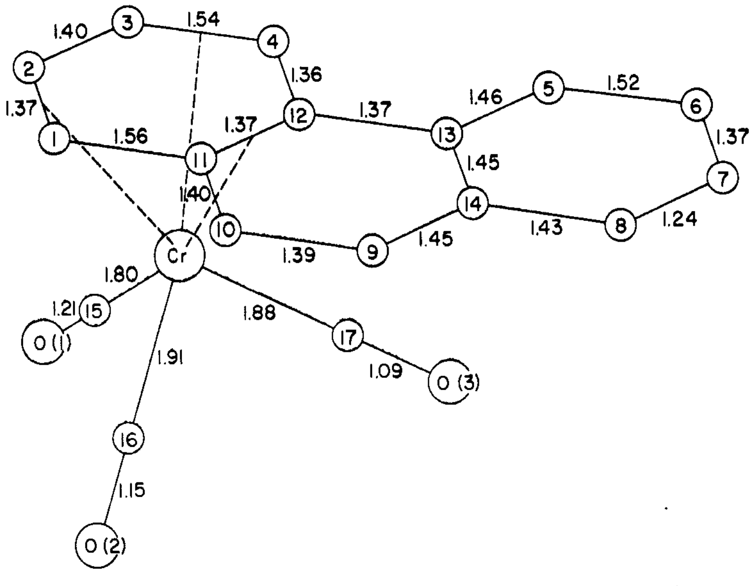


FIG. 16. The molecular structure of (phenanthrene)Cr$(CO)_3$ [from Deuschl and Hoppe (*93*)].

Splitting of the infrared-active *E* mode, degenerate if only the local symmetry of the Cr$(CO)_3$ system is considered (Section II,B), is observed in solution for the derivatives of condensed aromatic systems (*141*). This has been attributed to the inhomogeneity of the p_π electron system in the ring.

D. π-COMPLEXES OF HETEROCYCLIC SYSTEMS

Heterocyclic aromatic systems bonded through a lone pair on the hetero atom, e.g., py, were among the first mixed complexes of the Group VIB carbonyls prepared (*166*, *170*). The analogous π-complexes defied preparation until much later because the donor function of the hetero atom has led to the preferential formation of coordinately bonded derivatives.

The first π-heterocyclic derivative prepared was the orange, diamagnetic (thiophene)$Cr(CO)_3$ (d. 145°), prepared through the direct reaction of thiophene and the carbonyl in a sealed tube (*125*). A recent X-ray study of this compound has confirmed the originally proposed structure; there is a three-point attachment of the Cr which possesses octahedral valency to the two olefinic bonds and a lone pair on sulfur (Fig. 17) (*15*).

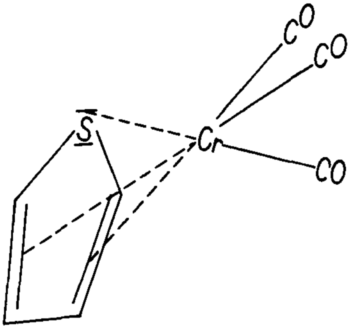


FIG. 17. The molecular structure (*schematic*) of (thiophene)$Cr(CO)_3$.

A π-derivative of *N*-methylpyridine was reported to have been prepared through the reaction of MepyI with the hexacarbonyl (*223*). The actual product, $[N\text{-Mepy}]^+[M(CO)_5I]^-$ (Section III), had been incorrectly formulated as π-*N*-MepyM$(CO)_3^+I^-$ (*126*). Interestingly enough, pyrolysis of the salt yielded small quantities of the red sublimable complex, π-2-MepyCr$(CO)_3$ (*126*); the suggested mechanism involves the formation of an iodine-bridged intermediate, followed by expulsion of HI and CO (*127*). The position of the methyl group was determined from infrared data. Attempts to prepare π-pyM$(CO)_3$ by pyrolysis of pyM$(CO)_5$ led only to the formation of py$_2$M$(CO)_4$ (*127*).

Attempts to synthesize the π-derivatives of pyrrole and furan have been unsuccessful (*127*).

The infrared spectra in the CO stretching region for these derivatives show a splitting of the *E* mode expected on the basis of the local symmetry of the carbonyl groups (*141*). As with condensed aromatic systems, the splitting has been attributed to the inhomogeneity of the π-aromatic system.

E. OLEFINIC DERIVATIVES

Group VIB metal carbonyl derivatives of cyclic di- and triolefins have been fully discussed in several excellent review articles (*34*, *139*, *140*, *151*) and will not be further discussed here. More recently, however, the preparation of π-complexes bonded through a single olefinic link has received considerable attention.

Direct displacement of CO from the hexacarbonyls by mono-olefins has resulted in the synthesis of a number of π-mono-olefinic derivatives, either monosubstituted or *trans*-disubstituted (Table XIV). The CO stretching frequencies for analogous derivatives decrease in the order ethylene > propylene > 2-butene, reflecting the inductive influence of substituents on the functional group (*276*). The complexes (butadiene)$W(CO)_5$ and *trans*-$(butadiene)_2W(CO)_4$ are of especial interest in light of the chelate *cis*-$(butadiene)_2Mo(CO)_2$, prepared by analogous methods reported by Fischer and co-workers (*116*). Formation of the latter complex may thus proceed through the initial displacement of two *trans* carbonyl groups by two butadiene molecules, followed by the displacement of *cis* carbonyls by the "nonbonded ends" of butadiene. It has been proposed that the cumulative charge-releasing effect of several olefinic bonds results in the *cis* orientation of CO groups in the chelated derivative (*276*).

TABLE XIV

SIMPLE π-OLEFINIC DERIVATIVES[a]

Complex	Color	M.P. (°C)	Physical data[b]	Ref.
$W(CO)_5$(butadiene)	White	—	3	(*276*)
trans-$W(CO)_4(\text{butadiene})_2$	Pale yellow	—	3	(*276*)
$W(CO)_5$(propylene)	Pale yellow	—	3	(*276*)
trans-$W(CO)_4$(propylene)	Pale yellow	—	3	(*276*)
trans-$Mo(CO)_3$(π-acrylonitrile)	—	—	3, 7	(*260, 320*)
trans-$W(CO)_3$(π-acrylonitrile)	Red	—	3, 7	(*260, 320*)
$W(CO)_5$(*trans*-stilbene)	Orange-red	135	—	(*321*)
$Mo(CO)_4(\text{1,2-diphenylacrylonitrile})_2$	Red	102–103 dec	3, 5	(*265*)

[a] Analogous derivatives, $M(CO)_{6-x}D_x$, of *trans*-2-butene ($x = 1$; M = W), *cis*-2-butene ($x = 1, 2$ *trans;* M = Mo, W), and ethylene ($x = 1, 2$ *trans;* M = Mo, W) were observed spectrally (*276*).

[b] See key to symbols (Table IV).

Acrylonitrile has received considerable attention as a ligand, because of two modes available for bonding: through the lone pair on nitrogen, or through the olefinic group in analogy to (acrylonitrile)$Fe(CO)_4$, in which the mode of attachment has been demonstrated through an X-ray study (*207*). Both modes of bonding are exhibited by Group VIB derivatives; monosubstituted and *cis*-disubstituted acrylonitrile derivatives are bonded through nitrogen's lone pair (Section II,D), while evidence indicates that

(1,2-diphenylacrylonitrile)$_2$Mo(CO)$_4$, and the *trans*-(acrylonitrile)$_3$M(CO)$_3$ (M = Mo, W), are π-bonded (*260, 265, 320*). The two types of complex have been distinguished through the positions of the CO and CC stretching frequencies, and through NMR studies, which indicate that the proton resonance pattern for acrylonitrile bonded through N differs little from that of unbonded acrylonitrile (*218*), while in the π-bonded derivative the pattern is greatly perturbed (*260, 320*). The *trans* tris complexes are interesting in that they are prepared from *cis*-(CH$_3$CN)$_3$M(CO)$_3$. The strong *trans* directing ability is undoubtedly a factor in the *trans* orientation of the ligands in this complex. As is true for py derivatives, for example, the donor function of N (until it is sufficiently inhibited by extensive ligand-to-metal charge donation) appears to predominate over the π-bonding function.

F. DERIVATIVES OF ACETYLENE

Metal carbonyls in general react with alkynes to give two types of complex, those in which the alkyne functions as a bridging group, and those in which the alkyne or a polymerization product is bonded to a single metal atom. Both types of derivative are represented among the Group VIB metal carbonyl complexes thus far reported.

As recently as 1959 it was reported that acetylenes gave no isolable products with Cr(CO)$_6$ and Mo(CO)$_6$ (*216*), and, although at about the same time Hübel and co-workers reported the preparation of tungsten carbonyl derivatives containing as many as six molecules of alkynes, no details were given (*175*). It was not until 1962 that the first Group VIB acetylenic derivatives were characterized (*229*).

Sheline *et al.* obtained CO stretching spectra characteristic of simple derivatives of the types M(CO)$_5$(alkyne) and *trans*-M(CO)$_4$(alkyne)$_2$ (Table XV) through the ultraviolet irradiation of solutions of hexacarbonyls and acetylenes. Attempts to isolate these products or more highly substituted derivatives failed, presumably because of the ultraviolet-induced polymerization of the alkynes; analogous alkene derivatives, however, were characterized (*276*).

Tate and co-workers (*319, 321*) and Strohmeier and von Hobe (*305*) have recently reported acetylenic derivatives of the type W(RCCR′)$_3$(CO) (Table XV), believed to be intermediates in the cyclization of alkynes, e.g., in the formation of hexamethylbenzene from diphenylacetylene (*237, 285, 305*). They have been prepared either directly through refluxing the carbonyl and acetylene in an appropriate solvent, or through displacement of ligands from complexes M(CO)$_3$D$_3$. Infrared and NMR data are consistent with a tetrahedral configuration in which all metal-acetylene bonds in these molecules are equivalent (Fig. 18) (*319, 321*). Sidgwick's rule requires that ten electrons be donated to the metal by the three alkyne

TABLE XV
REACTION PRODUCTS OF $M(CO)_6$ AND ACETYLENES[a]

Compound	Color	M.P. (°C)	Physical data[b]	Ref.
$(EtCCEt)_3W(CO)$	Yellow	55–56	3, 5, 7	(*319, 321*)
$(\phi CC\phi)_3W(CO)$	Yellow	193	3, 5, 7	(*305, 321*)
$(\phi CC\phi)_3Mo(CO)$	—	150	3	(*305*)
$(MeCC\phi)_3W(CO)$	Light yellow	96–98	3, 5, 7	(*321*)
$(\phi_4C_4)_2Mo(CO)_2$	Bright yellow	255–262	3	(*176*)
$(\phi_4C_4)(\phi CC\phi)Mo_2(CO)_4$	Green	200–205	3, 5	(*176*)
$(\phi_4C_4)(\phi_4C_5O)Mo(CO)_2$	Yellow	240–293	3	(*176*)
$(\phi_4C_4)(\phi CC\phi)_2Mo(CO)$	Violet	200–202	3, 5	(*176*)
$(\phi_5C_5)_2Mo$	Red	285–290	3, 5	(*176*)
$(\phi_5C_5)_2MoBr_3$	Green	—	5	(*176*)
$[CpMo(CO)_2]_2C_2\phi_2$	—	—	—	(*229*)
$[CpMo(CO)_2]_2HC_2\phi$	—	138–139	—	(*229*)
$(1,2,3,4\text{-}\phi_4C_6H_2)MoCp$ (?)	Brown	207	—	(*229*)

[a] Derivatives $W(CO)_{6-x}(acetylene)_x$; acetylene = CHCH ($M = W$; $x = 1, 2$), acetylene = CH_3CCH ($M = Mo, W$; $x = 1$), acetylene = EtCCEt ($M = Mo, W$; $x = 1$), were observed spectrophotometrically (*276*).

[b] See key to symbols (Table IV).

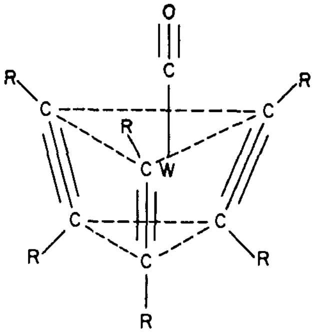


FIG. 18. The proposed structure of $(Et_2C_2)_3W(CO)$ [from Tate *et al.* (*321*)].

ligands, e.g., four each by two, and two by the third. It has been proposed, to explain the equivalence of the three metal-acetylene bonds, that the additional acetylenic electron pair occupies a nonbonding ligand molecular orbital of a'_2 symmetry (Fig. 19) (*321*).

Similar preparative techniques employing diphenylacetylene as a reactant with $Mo(CO)_6$ have yielded a second type of product, carbonyl derivatives containing tetraphenylcyclobutadiene groups (Table XV) (*176*). The structures proposed for these complexes (Fig. 20) have been

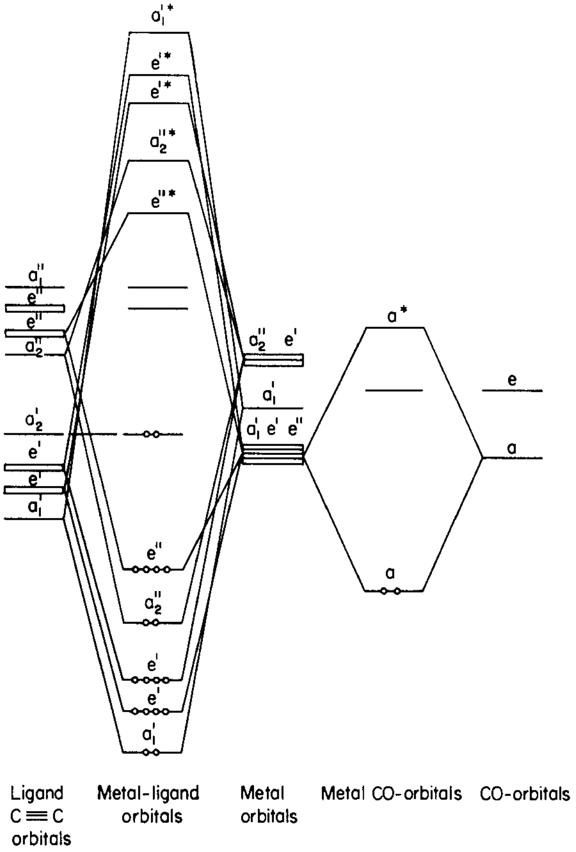


FIG. 19. Schematic molecular orbital energy-level diagram for $(Et_2C_2)_3W(CO)$ [from D. P. Tate *et al.* (*321*)].

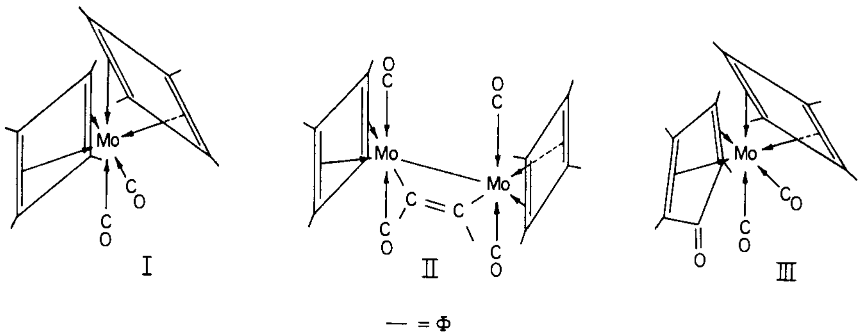
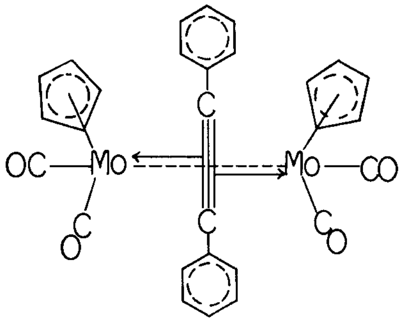


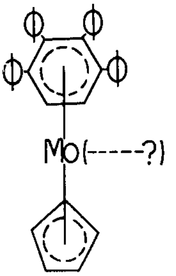
FIG. 20. Proposed structures for (I) $(\phi_4C_4)_2Mo(CO)_2$; (II) $(\phi_4C_4)_2(\phi C_2\phi)Mo_2(CO)_4$; (III) $(\phi_4C_4)(\phi_4C_5O)Mo(CO)_2$ [from Hübel and Merényi (*176*)].

inferred on the basis of infrared evidence and degradation products obtained upon their thermal decomposition. It will be noted that structure II in Fig. 20 contains an acetylenic bridging group. In addition, noncarbonyl-containing, paramagnetic bis(pentaphenylcyclopentadienyl)Mo has been isolated. Reactions of $CpMoMe(CO)_3$, $CpMoH(CO)_3$, or $[CoMo(CO)_3]_2$ with diphenylacetylene give a bridged acetylenic derivative formulated as



(43)

Phenylacetylene reacts with $CpMoMe(CO)_3$ to give an analogous derivative (*229*). $CpMoEt(CO)_3$, on the other hand, reacts with diphenylacetylene to give a product reported, on the basis of infrared data and chemical analysis, to be



(44)

in which the ethyl group and two diphenylacetylene molecules are incorporated into the benzene ring. The proposed structure violates Sidgwick's rule, and future investigations (molecular weight and magnetic susceptibility determinations, and proton magnetic resonance spectrum) may well show it to be a binuclear derivative or possibly a mononuclear hydride.

Although mechanisms have been proposed for the cyclic polymerization of acetylenic compounds (*176*, *229*), it is evident that much work remains to be done before the nature of such reactions is fully understood.

V. Prospects

It can be seen that a great deal of work has been done with the Group VIB metal carbonyls in a short period of time. Aside from future synthetic studies, the fields of infrared, visible, and ultraviolet spectroscopy and X-ray crystallography appear to offer interesting possibilities for further study. There appears to be little doubt that relationships between infrared spectra and bonding can be refined. X-ray studies of selected complexes, from which metal-ligand and metal-carbon bond lengths could be obtained, might contribute greatly to the realization of this goal and provide an answer to the question of the relative extent of σ- and π-bonding in specific complexes. There has, as yet, been no systematic study of the ultraviolet and visible spectra of simple substitution products $M(CO)_{6-x}D_x$. For example, the color of complexes can be correlated, in a rough way, to the π-accepting abilities of substituent groups (many derivatives in which ligand π-accepting ability is appreciable, e.g., certain phosphines and isocyanides are colorless, while amine derivatives are uniformly yellow) and to steric factors (many derivatives of bulky phosphines are yellow, while those of phosphines which should exert little steric influence are often colorless). What relative contributions these and other factors make to ultraviolet and visible spectra should prove to be of interest.

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REFERENCES

1. Abel, E. W., *Quart. Rev.* (*London*) **17**, 133 (1963).
*2. Abel, E. W., Bennett, M. A., Burton, R., and Wilkinson, G., *J. Chem. Soc.* p. 4559 (1958). Cycloheptatriene derivatives.
*3. Abel, E. W., Bennett, M. A., and Wilkinson, G., *Proc. Chem. Soc.* p. 152 (1958). Cycloheptatriene derivatives.
4. Abel, E. W., Bennett, M. A., and Wilkinson, G., *J. Chem. Soc.* p. 2323 (1959).
5. Abel, E. W., Bennett, M. A., and Wilkinson, G., *Chem. Ind.* (*London*) p. 442 (1960).
6. Abel, E. W., and Butler, I. S., *Abstr. Papers, 147th Meeting, Am. Chem. Soc., Phila.* p. 2L (1964).
7. Abel, E. W., Butler, I. S., and Reid, J. G., *J. Chem. Soc.* p. 2068 (1963).
8. Abel, E. W., Singh, A., and Wilkinson, G., *Chem. Ind.* (*London*) p. 1067 (1959).
9. Abel, E. W., Singh, A., and Wilkinson, G., *J. Chem. Soc.* p. 1321 (1960).

* Papers not explicitly mentioned in text or tables. Most have been reviewed elsewhere, or were too recent for inclusion.

10. Adams, D. M., *J. Chem. Soc.* p. 1771 (1964).

11. Allegra, G., *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.* **31,** 241 (1961).

12. Allegra, G., *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.* **31,** 399 (1961).

*13. Armstrong, V. S., and Prout, C. K., *J. Chem. Soc.* p. 3770 (1962). X-ray study of (cycloocta 1,3,5-trienyl)Cr(CO)$_3$.

*14. Avram, M., Sliam, E., and Nenitzescu, C. D., *Ann. Chem.* **636,** 184 (1960). (7,8-dimethyl tricyclodecadiene)Mo(CO)$_4$.

15. Bailey, M. F., and Dahl, L. F., *Abstr. Papers, 148th Meeting, Am. Chem. Soc.* pp. 29–30 (1964); *Chem. Eng. News,* **42,** no. 38, 50 (1964).

*16. Bamford, C., and Finch, C., *Trans Faraday Soc.* **59,** 118 (1963). Initiation of polymerization by M(CO)$_6$.

*17. Barinskii, R. L., and Nadzhakov, E. G., *Isv. Akad. Nauk SSSR, Ser. Fiz.* **24,** 407 (1960). K-edge absorption for Cr(CO)$_6$.

18. Barraclough, C. C., Lewis, J., and Nyholm, J., *J. Chem. Soc.* p. 2582 (1961).

19. Basolo, F., and Wojcicki, A., *J. Am. Chem. Soc.* **83,** 520 (1961).

*20. Baumgärtner, F., Fischer, E. O., and Zahn, N., *Naturwissenschaften* **49,** 156A (1962). CpTc(CO)$_3$ from (CpMo(CO)$_3$)$_2$.

21. Baumgärtner, F., and Zahn, N., *Z. Elektrochem.* **64,** 1046 (1960).

*22. Beck, W., and Nitzschmann, R. E., *Z. Naturforsch.* **17b,** 577 (1962). IR intensity measurements, M(CO)$_6$.

*23. Behrens, H., *Z. Naturforsch.* **7b,** 321 (1952). Failure to prepare carbonyl hydrides.

24. Behrens, H., and Anders, N., *Z. Naturforsch.* **19b,** 767 (1964).

25. Behrens, H., and Haag, W., *Z. Naturforsch.* **14b,** 600 (1959).

26. Behrens, H., and Haag, W., *Chem. Ber.* **94,** 312 (1961).

27. Behrens, H., and Haag, W., *Chem. Ber.* **94,** 320 (1961).

28. Behrens, H., and Harder, N., *Chem. Ber.* **97,** 426 (1964).

29. Behrens, H., and Harder, N., *Chem. Ber.* **97,** 433 (1964).

30. Behrens, H., and Klek, W., *Z. Anorg. Allgem. Chem.* **292,** 151 (1957).

31. Behrens, H., and Köhler, J., *Z. Anorg. Allgem. Chem.* **300,** 51 (1959).

32. Behrens, H., and Köhler, J., *Z. Anorg. Allgem. Chem.* **306,** 94 (1960).

33. Behrens, H., and Köhler, J., *Z. Naturforsch.* **14b,** 463 (1959).

34. Behrens, H., and Schwab, R., *Z. Naturforsch.* **19b,** 768 (1964).

35. Behrens, H., and Vogl, J., *Chem. Ber.* **96,** 2220 (1963).

36. Behrens, H., and Weber, R., *Z. Anorg. Allgem. Chem.* **291,** 122 (1957).

37. Behrens, H., and Zizlsperger, H., *Z. Naturforsch.* **16b,** 349 (1961).

38. Benlain, D., and Bigorgne, M., *Bull. Soc. Chim. France* p. 1583 (1963).

39. Bennett, M. A., *Chem. Rev.* **62,** 611 (1962).

*40. Bennett, M. A., Pratt, L., and Wilkinson, G., *J. Chem. Soc.* p. 2037 (1961). (Cycloheptatriene)Mo(CO)$_3$ derivatives.

*41. Bennett, M. A., and Wilkinson, G., *Chem. Ind. (London)* p. 1516 (1959). (Cycloocta 1,5-diene)Mo(CO)$_4$.

41a. Bertelli, P. J., Ph.D. Thesis, Univ. of Washington, Seattle, Washington, 1961.

41b. Bigorgne, M., Personal communication (1965).

42. Bigorgne, M., *J. Organometal. Chem.* **1,** 101 (1963).

43. Bigorgne, M., *J. Inorg. Nucl. Chem.* **26,** 107 (1964).

*44. Bigorgne, M., *J. Organometal. Chem.* **2,** 68 (1964). Competition of ligands with the metal of complexes.

44a. Bigorgne, M., and Messier, C. *J. Organometal. Chem.* **2,** 79 (1964).

45. Bigorgne, M., and Rassat, L., *Bull. Soc. Chim. France* p. 295 (1963).

*46. Boke, K., *Z. Physik. Chem. (Frankfurt)* [N.S.] **10,** 59 (1957). K-edge absorption for $Cr(CO)_6$.

*47. Böke, K., *Z. Physik. Chem. (Frankfurt)* [N.S.] **11,** 326 (1957). K-edge absorption for $CpCr(CO)_2NO$.

47a. Bonati, F., and Wilkinson, G., *J. Chem. Soc.* p. 179 (1964).

48. Booth, G., *Advan. Inorg. Chem. Radiochem.* **6,** 1 (1964).

49. Bor, G., *Spectrochim. Acta* **18,** 817 (1962).

50. Bouquet, G., and Bigorgne, M., *Bull. Soc. Chim. France* p. 433 (1962).

*51. Brown, D. A., *Chem. Ind. (London)*, p. 126 (1959). Bonding in (azulene)$M(CO)_3$.

*52. Brown, D. A., *J. Inorg. Nucl. Chem.* **10,** 39 (1959). Bonding in "half sandwich" $C_nH_nMY_m$ complexes.

*53. Brown, D. A., *J. Inorg. Nucl. Chem.* **10,** 49 (1959). On existence of metal-organic complexes containing hetero atoms.

53a. Brown, D. A., Gogan, N. J., and Sloan, H., *J. Chem. Soc.* p. 6873 (1965).

54. Brown, D. A., and Sloan, H., *J. Chem. Soc.* p. 3849 (1962).

55. Burton, R., Pratt, L., and Wilkinson, G., *J. Chem. Soc.* p. 4290 (1960).

56. Burton, R., and Wilkinson, G., *Chem. Ind. (London)* p. 1205 (1958).

57. Cais, M., and Feldkimel, M., *Tetrahedron Letters* p. 440 (1961).

58. Cais, M., and Feldkimel, M., *Tetrahedron Letters* p. 444 (1961).

59. Calderazzo, F., Ercoli, R., and Mangini, A., *Ric. Sci.* **29,** 2615 (1959).

60. Calderazzo, F., Tettamanti, G. C., and Ercoli, R., *Chim. Ind. (Milan)* **44,** 24 (1962).

61. Canziani, F., Zingales, F., and Sartorelli, N., *Gazz. Chim. Ital.* **94,** 841 (1964).

*62. Chatt, J., *Nature* **165,** 637 (1950). Bonding in PF_3 complexes.

63. Chatt, J., Guy, R. G., and Watson, H. R., *J. Chem. Soc.* p. 2332 (1961).

64. Chatt, J., Pauson, P. L., and Venanzi, L. M., *in* "Organometallic Chemistry" (H. Zeiss, ed.), p. 468. New York, Reinhold, 1960.

65. Chatt, J., and Thompson, D. T., *J. Chem. Soc.* p. 2713 (1964).

66. Chatt, J., and Thornton, D. A., *J. Chem. Soc.* p. 1005 (1964).

*67. Chatt, J., and Watson, H. R., *J. Chem. Soc.* p. 2545 (1962). Direct preparation of (ditertiary phosphine)$_3$M complexes.

68. Chatt, J., and Watson, H. R., *J. Chem. Soc.* p. 4980 (1961).

69. Chatt, J., and Watson, H. R., *Proc. Chem. Soc.* p. 243 (1960).

*70. Chatt, J., and Watson, H. R., *Nature* **189,** 1003 (1961). Direct preparation of (ditertiary phosphine)$_3$M complexes.

71. Coffey, C. E., *J. Am. Chem. Soc.* **83,** 1623 (1961). ϕ_4C_2 from $W(CO)_4$ dipy and $Cl_2\phi_2C$.

71a. Coffey, C. E., *J. Inorg. Nucl. Chem.* **25,** 179 (1963).

71b. Coffield, T. H., Kozikowski, J., and Clossen, R. D., *Chem. Soc. (London) Spec. Publ.* **13,** 126 (1959).

72. Cordes, J. F., and Schreiner, S., *Z. Anorg. Allgem. Chem.* **299,** 87 (1959).

73. Corradini, P., and Allegra, G., *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.* **26,** 511 (1959).

74. Corradini, P., and Allegra, G., *J. Am. Chem. Soc.* **81,** 2271 (1959).

75. Corradini, P., and Allegra, G., *J. Am. Chem. Soc.* **82,** 2075 (1960).

76. Cotton, F. A., *Inorg. Chem.* **3,** 702 (1964).

77. Cotton, F. A., and Kraihanzel, C. S., *J. Am. Chem. Soc.* **84,** 4432 (1962).

*78. Cotton, F. A., Liehr, A. O., and Wilkinson, G., *J. Inorg. Nucl. Chem.* **1,** 175 (1955). Cp metal carbonyl derivatives.

79. Cotton, F. A., and McCleverty, J. A., *Inorg. Chem.* **3,** 1398 (1964).

*80. Cotton, F. A., and Wilkinson, G., *Z. Naturforsch.* **9b,** 417 (1954). $[CpCr(CO)_3]_2$.

81. Cotton, F. A., and Zingales, F., *Chem. Ind.* (*London*) p. 149 (1960).

82. Cotton, F. A., and Zingales, F., *J. Am. Chem. Soc.* **83,** 351 (1961).

83. Cotton, F. A., and Zingales, F., *Inorg. Chem.* **1,** 145 (1962).

84. Cousins, M., and Green, M. L. H., *J. Chem. Soc.* p. 889 (1963).

85. Craig, D. P., Maccoll, A., Nyholm, R. S., Orgel, L. A., and Sutton, L. E., *J. Chem. Soc.* p. 332 (1954).

86. Cram, D. J., and Wilkinson, D. I., *J. Am. Chem. Soc.* **82,** 5721 (1960).

87. Cullen, W. R., and Hayter, R. C., *J. Am. Chem. Soc.* **86,** 1030 (1964).

88. Dahl, L. F., and Wei, C. H., *Inorg. Chem.* **2,** 328 (1963).

88a. Danti, A., and Cotton, F. A., *J. Chem. Phys.* **26,** 736 (1958).

*89. Dauben, H. L., Jr., and Honnen, L. R., *J. Am. Chem. Soc.* **80,** 5570 (1958).(π-Tropylium)$Mo(CO)_3^+$ BF_4^-.

89a. Davison, A., Edelstein, N., Holm, R., and Maki, A. H., *J. Am. Chem. Soc.* **86,** 2799 (1964).

90. Davison, A., McCleverty, J. A., and Wilkinson, G., *J. Chem. Soc.* p. 1133 (1963).

91. Davison, A., McFarlane, W., Pratt, L., and Wilkinson, G., *J. Chem. Soc.* p. 3653 (1962).

92. Davison, A., and Wilkinson, G., *Proc. Chem. Soc.* p. 356 (1960).

93. Deuschl, H., and Hoppe, W., *Acta Cryst.* **17,** 800 (1964).

93a. Dobson, G. R., *Inorg. Chem.* **4,** 1673 (1965).

94. Dobson, G. R., *J. Phys. Chem.* **69,** 677 (1965).

95. Dobson, G. R., El Sayed, M. A., Stolz, I. W., and Sheline, R. K., *Inorg. Chem.* **1,** 526 (1962).

95a. Doedens, R. J., and Dahl, L. W., *J. Am. Chem. Soc.* **87,** 2576 (1965).

*96. Dunitz, J. D., and Pauling, P., *Helv. Chim. Acta* **43,** 2188 (1960). Crystal structure of $(\pi\text{-}C_7H_8)Mo(CO)_3$.

97. El Sayed, M. A., *J. Phys. Chem.* **68,** 433 (1964).

98. El Sayed, M. A., and Kaesz, H. D., *J. Mol. Spectroy.* **9,** 310 (1962).

99. Ercoli, R., Calderazzo, F., and Albertola, A., *Chim. Ind.* (*Milan*) **41,** 975 (1959).

100. Ercoli, R., Calderazzo, F., and Mantica, E., *Chim. Ind.* (*Milan*) **41,** 404 (1959).

101. Ercoli, R., and Mangini, A., *Ric. Sci.* **28,** 2136 (1958).

102. Fischer, E. O., *Angew. Chem.* **67,** 475 (1955).

103. Fischer, E. O., *J. Inorg. Nucl. Chem.* **8,** 268 (1958).

104. Fischer, E. O., *Abstr. Papers, 147th Meeting Am. Chem. Soc., Phila.* p. 1L (1964).

*105. Fischer, E. O., Beckert, O., Hafner, W., and Stahl, H. O., *Z. Naturforsch.* **10b,** 598 (1955). Cp metal carbonyl nitrosyls.

106. Fischer, E. O., and Fichtel, K., *Chem. Ber.* **94,** 1200 (1961).

107. Fischer, E. O., Fichtel, K., and Öfele, K., *Chem. Ber.* **95,** 249 (1962).

108. Fischer, E. O., and Fritz, H. P., *Advan. Inorg. Chem. Radiochem.* **1,** 55 (1959).

109. Fischer, E. O., and Fritz, H. P., *Angew. Chem.* **73,** 353 (1961).

*110. Fischer, E. O., and Fröhlich, W., *Chem. Ber.* **92,** 2995 (1959). (Cycloocta 1,5-diene)$M(CO)_4$.

*111. Fischer, E. O., and Fröhlich, W., *Z. Naturforsch.* **15b,** 266 (1960). Bis(1,3-cyclohexadiene)$Mo(CO)_2$.

*112. Fischer, E. O., and Hafner, W., *Z. Naturforsch.* **10b,** 140 (1955). $CpCrH(CO)_3$.

*113. Fischer, E. O., Hafner, W., and Stahl, H. O., *Z. Anorg. Allgem. Chem.* **282,** 47 (1955). $CpMH(CO)_3$.

*114. Fischer, E. O., Joos, G., and Meer, W., *Z. Naturforsch.* **13b,** 456 (1958). Magnetic data on $ArM(CO)_3$.

*115. Fischer, E. O., and Kögler, H. P., *Angew. Chem.* **68**, 462 (1956). $[Cr(C_6H_6)_2]^+$-$[CpCr(CO)_3]^-$.

116. Fischer, E. O., Kögler, H. P., and Küzel, P., *Chem. Ber.* **93**, 3006 (1960).

117. Fischer, E. O., and Kriebitzsch, N., *Z. Naturforsch.* **15b**, 565 (1960).

118. Fischer, E. O., Kriebitzsch, N., and Fischer, R. D., *Chem. Ber.* **92**, 3214 (1959).

119. Fischer, E. O., and Küzel, P., *Z. Naturforsch.* **16b**, 475 (1961).

120. Fischer, E. O., and Küzel, P., *Z. Anorg. Allgem. Chem.* **317**, 226 (1962).

*121. Fischer, E. O., and Leipfinger, H., *Z. Naturforsch.* **10b**, 353 (1955). Magnetic data, Cp metal carbonyls and nitrosyls.

122. Fischer, E. O., and Maasböl, A., *Angew. Chem. Intern. Ed. English* **3**, 580 (1964).

123. Fischer, E. O., and Moser, E., *J. Organometal. Chem.* **2**, 230 (1964).

124. Fischer, E. O., and Öfele, K., *Chem. Ber.* **90**, 2532 (1957).

125. Fischer, E. O., and Öfele, K., *Chem. Ber.* **91**, 2395 (1958).

126. Fischer, E. O., and Öfele, K., *Z. Naturforsch.* **14b**, 736 (1959).

127. Fischer, E. O., and Öfele, K., *Chem. Ber.* **93**, 1156 (1960).

128. Fischer, E. O., Öfele, K., Essler, H., Fröhlich, W., Mortensen, G. P., and Semmlinger, W., *Z. Naturforsch.* **13b**, 458 (1958).

129. Fischer, E. O., Öfele, K., Essler, H., Fröhlich, W., Mortensen, G. P., and Semmlinger, W., *Chem. Ber.* **91**, 2763 (1958).

*130. Fischer, E. O., and Palm, C., *Z. Naturforsch.* **14b**, 347 (1959). (Cyclooctatriene)-$M(CO)_3$ derivatives.

*131. Fischer, E. O., Palm, C., and Fritz, H. P., *Chem. Ber.* **92**, 2645 (1959). (Cyclooctatriene)$M(CO)_3$.

*132. Fischer, E. O., and Piesbergen, W., *Z. Naturforsch.* **11b**, 758 (1956). Magnetic susceptibilities of Cp derivatives.

133. Fischer, E. O., and Plesske, K., *Chem. Ber.* **94**, 93 (1961).

134. Fischer, E. O., and Schreiner, S., *Chem. Ber.* **92**, 938 (1959).

135. Fischer, E. O., and Semmlinger, W., *Naturwissenschaften* **48**, 525 (1961).

136. Fischer, E. O., and Ulm, K., *Chem. Ber.* **94**, 2413 (1961).

137. Fischer, E. O., and Ulm, K., *Z. Naturforsch.* **15b**, 59 (1960).

138. Fischer, E. O., and Ulm, K., *Z. Naturforsch.* **16b**, 757 (1961).

139. Fischer, E. O., and Werner, H., *Angew. Chem.* **75**, 57 (1963).

140. Fischer, E. O., and Werner, H., *Angew Chem. Intern. Ed. English* **2**, 80.

141. Fischer, R. D., *Chem. Ber.* **93**, 165 (1960).

*142. Fischer, R. D., *Z. Naturforsch.* **18a**, 1373B (1963). Ring charge and size effects for $ArM(CO)_3$.

143. Fowles, G. W. A., and Jenkins, D. K., *Inorg. Chem.* **3**, 257 (1964).

144. Fritz, H. P., Keller, H., and Fischer, E. O., *Naturwissenschaften* **48**, 518 (1961).

145. Fritz, H. P., and Manchot, J., *Spectrochim. Acta* **18**, 171 (1962).

146. Fritz, H. P., and Manchot, J., *Z. Naturforsch.* **17b**, 711 (1962).

146a. Ganorkar, M. C., and Stiddard, M. H. B., *Chem. Commun.* p. 22 (1965).

147. Gerrard, W., Lappert, M. F., Pyszora, H., and Wallis, J. W., *J. Chem. Soc.* p. 2182 (1960).

148. Goan, J. C., Huether, C. H., and Podall, H. E., *Inorg. Chem.* **2**, 1078 (1963).

148a. Gray, H. B., personal communication, 1965.

149. Gray, H. B., and Beach, N. A., *J. Am. Chem. Soc.* **85**, 2922 (1963).

150. Green, M. L. H., and Stear, A. N., *J. Organometal. Chem.* **1**, 230 (1964).

151. Guy, R. G., and Shaw, B. L., *Advan. Inorg. Chem. Radiochem.* **4**, 78 (1962).

152. Hansen, A. W., *Acta Cryst.* **15**, 930 (1962).

153. Hayter, R. G., *Inorg. Chem.* **2**, 1031 (1963).

154. Hayter, R. G., *Inorg. Chem.* **3,** 711 (1964).
155. Herberich, C. E., and Fischer, E. O., *Chem. Ber.* **95,** 2803 (1962).
156. Herzog, S., and Taube, R., *Z. Chem.* **2,** 208 (1962).
157. Hieber, W., and Abeck, W., *Z. Naturforsch.* **7b,** 320 (1952).
158. Hieber, W., Abeck, W., and Platzer, H. K., *Z. Anorg. Allgem. Chem.* **280,** 241 (1955).
159. Hieber, W., Abeck, W., and Platzer, H. K., *Z. Anorg. Allgem. Chem.* **280,** 252 (1955).
160. Hieber, W., Beck, W., and Braun, G., *Angew. Chem.* **72,** (1960).
161. Hieber, W., and Englert, K., *Z. Anorg. Allgem. Chem.* **300,** 311 (1959).
162. Hieber, W., Englert, K., and Rieger, K., *Z. Anorg. Allgem. Chem.* **300,** 295 (1959).
163. Hieber, W., Englert, K., and Rieger, K., *Z. Anorg. Allgem. Chem.* **300,** 304 (1959).
164. Hieber, W., and Floss, J. G., *Z. Anorg. Allgem. Chem.* **291,** 314 (1957).
165. Hieber, W., and Kruck, T., *Z. Naturforsch.* **16b,** 709 (1961).
166. Hieber, W., and Mühlbauer, F., *Z. Anorg. Allgem. Chem.* **221,** 337 (1935).
167. Hieber, W., and Peterhans, J., *Z. Naturforsch.* **14b,** 462 (1959).
168. Hieber, W., and von Pigenot, D., *Chem. Ber.* **89,** 616 (1956).
169. Hieber, W., and Rieger, K., *Z. Anorg. Allgem. Chem.* **300,** 288 (1959).
170. Hieber, W., and Romberg, E., *Z. Anorg. Allgem. Chem.* **221,** 349 (1935).
171.* Hieber, W., and Scharfenberg, C., *Ber. Deut. Chem. Ges.* **73, 1012 (1940). Reported $(C_6H_5S)Mo(CO)_2py$ complex.
172.* Hieber, W., and Weiss, A., *Z. Anorg. Allgem. Chem.* **287, 223 (1956). Dipole moment, $CpCr(CO)_2NO$.
173. Hoberman, P., M.S. thesis, Florida State Univ., Tallahassee, Florida, 1964.
174. Houk, L. W., and Dobson, G. R., unpublished results, 1964.
175. Hübel, W., Braye, E. H., Clauss, A., Weiss, E., Krüerke, N., Brown, D. A., King, G.S.D., and Hoogzand, C., *J. Inorg. Nucl. Chem.* **9,** 204 (1959).
176. Hübel, W., and Merényi, R., *J. Organometal. Chem.* **2,** 213 (1964).
177. Huber, M., and Poilblanc, R., *Bull. Soc. Chim. France* p. 1019 (1960).
178. Humphrey, R. E., *Spectrochim. Acta* **17,** 93 (1961).
179. Jackson, W. R., Nicholls, B., and Whiting, M. C., *J. Chem. Soc.* p. 469 (1960).
179a. Jones, L. H., *J. Mol. Spectry.* **9,** 130 (1962).
179b. Jones, L. H., *J. Chem. Phys.* **36,** 2375 (1962).
180. Jones, L. H., personal communication, 1964.
181. Joshi, K. K., Pauson, P. L., and Stubbs, W. H., *J. Organometal. Chem.* **1,** 51 (1963).
181a. Kaesz, H. D., King, R. B., and Stone, F. C. A., *Z. Naturforsch.* **15b,** 763 (1960).
181b. Kettle, S. F. A., *Inorg. Chem.* **4,** 1661 (1965).
182. King, R. B., *Inorg. Chem.* **2,** 641 (1963).
183. King, R. B., *Inorg. Chem.* **2,** 936 (1963).
184. King, R. B., *J. Am. Chem. Soc.* **85,** 1587 (1963).
185. King, R. B., *Inorg. Chem.* **3,** 1039 (1964).
185a. King, R. B., and Bisnette, M. B., *Tetrahedron Letters* p. 1137 (1963).
185b. King, R. B., *Advan. Organometal. Chem.* **2,** 157 (1964).
186. King, R. B., and Bisnette, M. B., *Inorg. Chem.* **3,** 785 (1964).
187. King, R. B., and Bisnette, M. B., *Inorg. Chem.* **3,** 801 (1964).
188. King, R. B., and Bisnette, M. B., *J. Am. Chem. Soc.* **86,** 1267 (1964).
189. King, R. B., and Bisnette, M. B., *J. Am. Chem. Soc.* **86,** 5694 (1964).
190. King, R. B., and Bisnette, M. B., *J. Organometal. Chem.* **2,** 15 (1964).
**191.* King, R. B., and Stone, F. G. A., *Chem. Ind.* (*London*) p. 232 (1960). (Bicyclo 4,3,0-nonatriene)$Mo(CO)_3$.

192. King, R. B., and Stone, F. G. A., *J. Am. Chem. Soc.* **83,** 4557 (1960).

*193. King, R. B., and Stone, F. G. A., *J. Am. Chem. Soc.* **83,** 3590 (1961). Derivatives of 5,6-dimethylene bicyclo 2,2,1 heptene-2.

194. King, R. B., Treichel, P. M., and Stone, F. G. A., *Chem. Ind. (London)* p. 747 (1961).

195. King, R. B., Treichel, P. M., and Stone, F. G. A., *Proc. Chem. Soc.* p. 69 (1961).

196. Kling, O., Nikolaiski, E., and Schläfer, H. L., *Ber. Bunsenges. Physik. Chem.* **67,** 883 (1963).

197. Kraihanzel, C. S., and Cotton, F. A., *Inorg. Chem.* **2,** 533 (1963).

198. Kruck, T., *Chem. Ber.* **97,** 2018 (1964).

199. Kruck, T., *Z. Naturforsch.* **19b,** 165 (1964).

200. Kruck, T., and Prasch, A., *Z. Naturforsch.* **19b,** 669 (1964).

201. Lewis, J., Nyholm, R. S., Pande, C. S., Sandhu, S. S., and Stiddard, M. H. B., *J. Chem. Soc.* p. 3009 (1964).

202. Lewis, J., Nyholm, R. S., Pande, C. S., and Stiddard, M. H. B., *J. Chem. Soc.* p. 3600 (1963).

*203. Liehr, A. D., *Naturwissenschaften* **44,** 61 (1957). Structure of $CpMH(CO)_3$.

204. Liptay, W., Strohmeier, W., and Hellmann, H., *Ber. Bunsenges. Physik. Chem.* **68,** 91 (1964).

205. Lundquist, R. R., and Cais, M., *J. Org. Chem.* **27,** 1167 (1962).

206. Lüttringhaus, A., and Kullick, W., *Tetrahedron Letters* **10,** 13 (1959).

207. Luxmoore, A. R., and Truter, M. R., *Acta Cryst.* **15,** 1117 (1962).

208. McCleverty, J. A., and Wilkinson, G., *J. Chem. Soc.* p. 4096 (1963).

209. Magee, T. D., Mathews, C. N., and Wang, T. S., *J. Am. Chem. Soc.* **83,** 3200 (1961).

*210. Malatesta, L., *Progr. Inorg. Chem.* **1,** 283 (1959). Review on isonitrile derivatives.

211. Malatesta, L., *Chim. Ind. (Milan)* **46,** 894 (1964).

212. Mandelbaum, A., Neuwirth, Z., and Cais, M., *Inorg. Chem.* **2,** 902 (1963).

213. Mannerskantz, H. C. E., and Wilkinson, G., *J. Chem. Soc.* p. 4454 (1962).

*214. Manuel, T. A., and Stone, F. G. A., *Chem. Ind. (London)* p. 1349 (1959). (1,5-cyclooctadiene)$W(CO)_4$.

*215. Manuel, T. A., and Stone, F. G. A., *Chem. Ind. (London)* p. 231 (1960). (Dimethyldivinylsilane)$W(CO)_4$.

216. Markby, R., Sternberg, H. W., and Wender, I., *Chem. Ind. (London,* p. 1381) (1959).

217. Mašek, J., Nyholm, R. S., and Stiddard, M. H. B., *Collection Czech. Chem. Commun.* **29,** 1714 (1964).

218. Massey, A. G., *J. Inorg. Nucl. Chem.* **24,** 1173 (1962).

219. Massey, A. G., and Orgel, L. E., *Chem. Ind. (London)* p. 436 (1961).

220. Massey, A. G., and Orgel, L. E., *Nature* **191,** 1387 (1961).

221. Matthews, C. N., Magee, T. D., and Wotiz, J. H., *J. Am. Chem. Soc.* **81,** 2273 (1959).

222. Modiano, A., Mandelbaum, A., and Cais, M., *Proc. 7th Intern. Conf. Coord. Chem., Stockholm, 1962* p. 303 (1962).

223. Moore, B., and Wilkinson, G., *Proc. Chem. Soc.* p. 61 (1959).

224. Mostardini, E., Calderazzo, F., and Ercoli, R., *Chim. Ind. (Milan)* **42,** 1231 (1960).

*225. Munro, J. D., and Pauson, P. L., *Proc. Chem. Soc.* p. 267 (1959). (Tropylium)-$M(CO)_3^+$.

*226. Munro, J. D., and Pauson, P. L., *J. Chem. Soc.* p. 3475 (1961). Cycloheptatriene and tropylium derivatives.

*227. Munro, J. D., and Pauson, P. L., *J. Chem. Soc.* p. 3479 (1961). Cycloheptatriene and tropylium derivatives.

228. Munro, J. D., and Pauson, P. L., *J. Chem. Soc.* p. 3484 (1961).

229. Nakamura, A., *Mem. Inst. Sci. Ind. Res. Osaka Univ.* **19,** 81 (1962).

230. Nast, R., and Kohl, H., *Z. Anorg. Allgem. Chem.* **320,** 135 (1963).

231. Nast, R., and Kohl, H., *Chem. Ber.* **97,** 207 (1964).

232. Natta, G., Ercoli, R., and Calderazzo, F., *Angew. Chem.* **70,** 322 (1958).

233. Natta, G., Ercoli, R., and Calderazzo, F., *Chim. Ind.* (*Milan*) **40,** 287 (1958).

234. Natta, G., Ercoli, R., Calderazzo, F., and Santambroglio, E., *Chim. Ind.* (*Milan*) **40,** 1003 (1958).

235. Nesmayanov, A. N., Anisinov, K. N., and Kolobova, N. E., *Dokl. Akad. Nauk SSSR* **156,** 612 (1964).

*236. Nesmayanov, A. N., Anisinov, K. N., Kolobova, N. E., and Beschastnov, A. S., *Dokl. Akad. Nauk SSSR* **159,** 377 (1964). Binuclear Cp carbonyl derivatives containing two different metals.

237. Nesmayanov, A. N., and Vol'kenau, N. A., *Izv. Akad. Nauk SSSR Otdel. Khim. Nauk* p. 367 (1961).

238. Nicholls, B., and Whiting, M. C., *Proc. Chem. Soc.* p. 152 (1958).

239. Nicholls, B., and Whiting, M. C., *J. Chem. Soc.* p. 551 (1959).

240. Nigam, H. L., and Nyholm, R. S., *Proc. Chem. Soc.* p. 321 (1957).

241. Nigam, H. L., Nyholm, R. S., and Stiddard, M. H. B., *J. Chem. Soc.* p. 1893 (1960).

242. Nigam, H. L., Nyholm, R. S., and Stiddard, M. H. B., *J. Chem. Soc.* p. 1806 (1960).

243. Orgel, L. E., "Introduction to Transition Metal Chemistry—Ligand Field Theory." Wiley, New York, 1960.

244. Orgel, L. E., *Inorg. Chem.* **1,** 25 (1962).

245. Pajaro, G., Calderazzo, F., and Ercoli, R., *Gazz. Chim. Ital.* **90,** 1486 (1960).

246. Pauson, P. L., *in* "Organometallic Chemistry" (H. Zeiss, ed.), p. 346. Reinhold, New York, 1960.

*247. Pauson, P., *Proc. Chem. Soc.* p. 297 (1960). Hydrocarbon metal carbonyls—a review.

248. Pettit, R., *J. Am. Chem. Soc.* **81,** 1266 (1959). Bicyclo-2,2,1-heptadiene derivatives.

*249. Piper, T. S., and Wilkinson, G., *Naturwissenschaften* **42,** 625 (1955). π-Cp derivatives.

*250. Piper, T. S., and Wilkinson, G., *J. Inorg. Nucl. Chem.* **3,** 104 (1956). $CpMR(CO)_3$ derivatives.

250a. Podall, H. E., and Iapalucci, T. L., *J. Polymer Sci., Pt. B* **1,** 457 (1963).

251. Poilblanc, R., dissertation, Univ. of Paris, 1963.

251a. Poilblanc, R., *Compt. Rend.* **256,** 4910 (1963).

252. Poilblanc, R., and Bigorgne, M., *Compt. Rend.* **250,** 1064 (1960).

253. Poilblanc, R., and Bigorgne, M., *Compt. Rend.* **252,** 3054 (1961).

254. Poilblanc, R., and Bigorgne, M., *Bull. Chim. Soc. France* p. 1301 (1962).

255. Randall, E. W., and Sutton, L. E., *Proc. Chem. Soc.* p. 93 (1959).

256. Reimschneider, R., Becker, R., and Franz, K., *Monatsh. Chem.* **90,** 571 (1959).

*257. Reynolds, L. T., and Wilkinson, G., *J. Inorg. Nucl. Chem.* **9,** 86 (1958). $CpMoMe(CO)_3$.

*258. Rhomberg, M. C., and Owen, B. B., *J. Am. Chem. Soc.* **73,** 5409 (1951). Supposed $Cr(CO)_5H_2$.

259. Richardson, J. W., *in* "Organometallic Chemistry" (H. Zeiss, ed.), p. 1. New York, Reinhold, 1960.

259a. Ross, E., and Dobson, G. R., unpublished results, 1965.

260. Ross, B. F., Grasselli, J. G., Ritchey, W. M., and Kaesz, H. D., *Inorg. Chem.* **2,** 1023 (1963).

260a. Rundle, R. E., and Goring, J. H., *J. Am. Chem. Soc.* **72,** 5773 (1950).

261. Schmutzler, R., *Advan. Chem. Ser.* **37,** 150 (1963).

262. Schmutzler, R., *Chem. Ber.* **96,** 2435 (1963).

263. Schmutzler, R., *Inorg. Chem.* **3,** 415 (1964).

264.* Schneider, A., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **31, 249 (1962). K-edge absorption for arene metal carbonyls.

265. Schrauzer, G. N., and Eichler, S., *Chem. Ind.* (*London*) p. 1270 (1961).

266. Schrauzer, G. N., Finck, H. W., and Mayweg, V., *Z. Naturforsch.* **19b,** 1080B (1964).

267.* Schwab, G. M., Fischer, E. O., and Voitländer, J., *Naturwissenschaften* **41, 228 (1954). On $[CpCr(CO)_3]_2$ incorrectly formulated as $Cp_2(CO)_5Cr_2$ in (329).

**268.* Setkina, V. N., Bargnetskaya, N. K., and Anisimov, K. N., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1873 (1964). Isotopic hydrogen exchange in (benzene)-$Cr(CO)_3$.

269. Seyferth, D., and Alleston, D. L., *Inorg. Chem.* **2,** 417 (1963).

270.* Shustorovich, E. M., *Zh. Strukt. Khim.* **3, 103 (1962). NO and CO bonding in transition metal compounds.

271. Stiddard, M. H. B., *J. Chem. Soc.* p. 4712 (1962).

272. Stiddard, M. H. B., *J. Chem. Soc.* p. 756 (1963).

273. Stolz, I. W., Dobson, G. R., and Sheline, R. K., *J. Am. Chem. Soc.* **84,** 3589 (1962).

274. Stolz, I. W., Dobson, G. R., and Sheline, R. K., *J. Am. Chem. Soc.* **85,** 1013 (1963).

275. Stolz, I. W., Dobson, G. R., and Sheline, R. K., *Inorg. Chem.* **2,** 323 (1963).

276. Stolz, I. W., Dobson, G. R., and Sheline, R. K., *Inorg. Chem.* **2,** 1264 (1963).

276a. Stolz, I. W., Haas, H., and Sheline, R. K., *J. Am. Chem. Soc.* **87,** 716 (1965).

277. Stone, F. G. A., *Chem. Rev.* **58,** 101 (1958).

278. Strohmeier, W., *Chem. Ber.* **94,** 2490 (1961).

279. Strohmeier, W., *Chem. Ber.* **94,** 3337 (1961).

280. Strohmeier, W., *Z. Naturforsch.* **17b,** 566 (1962).

281. Strohmeier, W., *Z. Naturforsch.* **17b,** 627 (1962).

282.* Strohmeier, W., *Angew. Chem.* **75, 1024 (1963). Toxicity of metal carbonyl derivatives.

283. Strohmeier, W., *Ber. Bunsenges. Physik. Chem.* **67,** 892 (1963).

284. Strohmeier, W., *Angew. Chem. Intern. Ed. English* **3,** 730 (1964).

285. Strohmeier, W., and Barbeau, C., *Z. Naturforsch.* **19b,** 262 (1964).

286.* Strohmeier, W., Barbeau, C., and von Hobe, D., *Chem. Ber.* **96, 3254 (1963). CO displacement by ligands coordinating through O.

287. Strohmeier, W., and Gerlach, K., *Chem. Ber.* **93,** 2087 (1960).

288. Strohmeier, W., and Gerlach, K., *Z. Naturforsch.* **15b,** 413 (1960).

289. Strohmeier, W., and Gerlach, K., *Z. Naturforsch.* **15b,** 622 (1960).

290. Strohmeier, W., and Gerlach, K., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **27,** 439 (1961).

291. Strohmeier, W., and Gerlach, K., *Chem. Ber.* **94,** 398 (1961).

292. Strohmeier, W., Gerlach, K., and von Hobe, D., *Chem. Ber.* **94,** 164 (1961).

293. Strohmeier, W., Gerlach, K., and Matthias, G., *Z. Naturforsch.* **15b,** 621 (1960).

294. Strohmeier, W., and Hellmann, H., *Ber. Bunsenges. Physik. Chem.* **67,** 190 (1963).

295. Strohmeier, W., and Hellmann, H., *Chem. Ber.* **96,** 2859 (1963).

296. Strohmeier, W., and Hellmann, H., *Z. Naturforsch.* **18b,** 769 (1963).

297. Strohmeier, W., and Hellmann, H., *Ber. Bunsenges. Physik. Chem.* **68,** 481 (1964).

298. Strohmeier, W., and Hellmann, H., *Chem. Ber.* **97,** 1877 (1964).

299.* Strohmeier, W., and Hellmann, H., *Z. Naturforsch.* **19b, 164 (1964). Relative acceptor strengths of M in metal carbonyls.

300. Strohmeier, W., and von Hobe, D., *Z. Elektrochem.* **64,** 945 (1960).

301. Strohmeier, W., and von Hobe, D., *Chem. Ber.* **94,** 761 (1961).

302. Strohmeier, W., and von Hobe, D., *Chem. Ber.* **94,** 2031 (1961).

303. Strohmeier, W., and von Hobe, D., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **34,** 393 (1962).

304. Strohmeier, W., and von Hobe, D., *Z. Naturforsch.* **18b,** 770 (1963).

305. Strohmeier, W., and von Hobe, D., *Z. Naturforsch.* **19b,** 959 (1964).

306. Strohmeier, W., von Hobe, D., Schönauer, G., and Laporte, H., *Z. Naturforsch.* **17b,** 502 (1962).

307. Strohmeier, W. and Langhauser, W., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **28,** 268 (1961).

308. Strohmeier, W., Mahgoub, H. G. S., and von Hobe, D., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **35,** 253 (1962).

309. Strohmeier, W., Matthias, G., and von Hobe, D., *Z. Naturforsch.* **15b,** 813 (1960).

310. Strohmeier, W., and Mittnacht, H., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **29,** 339 (1961).

311. Strohmeier, W., and Mittnacht, H., *Chem. Ber.* **93,** 2085 (1963).

312. Strohmeier, W., and Mittnacht, H., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **34,** 82 (1962).

313. Strohmeier, W., and Müller, R., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **28,** 112 (1961).

314. Strohmeier, W., and Müller, R., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **40,** 85 (1964).

315. Strohmeier, W., and Schönauer, G., *Chem. Ber.* **94,** 1346 (1961).

316. Strohmeier, W., and Schönauer, G., *Chem. Ber.* **95,** 1767 (1962).

317. Strohmeier, W., and Starrico, E. H., *Z. Physik. Chem.* (*Frankfurt*) [N.S.] **38,** 315 (1963).

318. Stucke, C., and Dobson, G. R., unpublished results, 1964.

319. Tate, D. P., and Augl, J. M., *J. Am. Chem. Soc.* **85,** 2174 (1963).

320. Tate, D. P., Augl, J. M., and Buss, H., *Inorg. Chem.* **2,** 427 (1963).

321. Tate, D. P., Augl, J. M., Ritchey, W. M., Ross, B. L., and Grasselli, J. G., *J. Am. Chem. Soc.* **86,** 3261 (1964).

322. Tate, D. P., Knipple, W. R., and Augl, M., *Inorg. Chem.* **1,** 433 (1962).

323. Treichel, P. M., Morris, J. H., and Stone, F. G. A., *J. Chem. Soc.* p. 720 (1963).

324. Tyler, J. K., Cox, A. P., and Sheridan, J., *Nature* **183,** 1182 (1959).

325.* Waugh, J. S., Loehlin, J. H., Cotton, F. A., and Shoemaker, D. P., *J. Chem. Phys.* **31, 1434 (1959). Rotation about M-Cp bond.

326.* Weiss, E., and Hübel, W., *J. Inorg. Nucl. Chem.* **11, 42 (1959).(Tetracyclone)$_2$-$Mo(CO)_2$.

327. Werner, R. P. M., *Chem. Ber.* **94,** 1207 (1961).

328. Werner, R. P. M., and Coffield, T. H., *Chem. Ind.* (*London*) p. 936 (1960).

329.* Wilkinson, G., *J. Am. Chem. Soc.* **76, 209 (1954). Cp derivatives.

330. Wilkinson, G., and Cotton, F. A., *Progr. Inorg. Chem.* **1,** 1 (1959).

331.* Willeford, B. R., and Fischer, E. O., *Naturwissenschaften* **51, 38 (1964). X-ray study of $[CpMo(CO)_3]_2$ and $[CpW(CO)_3]_2$.

*332. Wilson, F. C., and Shoemaker, D. P., *Naturwissenschaften* **43,** 57 (1956). X-ray study of $[CpMo(CO)_3]_2$.
333. Wilson, F. C., and Shoemaker, D. P., *J. Chem. Phys.* **27,** 809 (1957).
334. Wojcicki, A., and Farona, M. F., *J. Inorg. Nucl. Chem.* **26,** 2289 (1964).
335. Woodward, L. A., and Hall, J. R., *Nature* **181,** 831 (1958).
336. Yamada, S., Yamasaki, H., Nishikawa, H., and Tsuchida, R., *Bull. Chem. Soc. Japan* **33,** 481 (1960).
337. Zeiss, H., *in* "Organometallic Chemistry" (H. Zeiss, ed.), p. 380. New York, Reinhold, 1960.
338. Zingales, F., and Canziani, F., *Gazz. Chim. Ital.* **92,** 343 (1962).
339. Zingales, F., Canziani, F., and Ugo, R., *Gazz. Chim. Ital.* **92,** 761 (1962).

SUPPLEMENTARY REFERENCES*

340. Bailey, M. F., and Dahl, L. F., *Inorg. Chem.* **4,** 1298 (1965). The structure of (hexamethylbenzene)$Cr(CO)_3$.
341. Bailey, M. F., and Dahl, L. F., *Inorg. Chem.* **4,** 1306 (1965). The structure of (thiophene)$Cr(CO)_3$.
342. Bailey, M. F., and Dahl, L. F., *Inorg. Chem.* **4,** 1314 (1965). Three dimensional crystal structure of (benzene)$Cr(CO)_3$.
343. Beck, W., and Lottes, K., *Chem. Ber.* **98,** 2657 (1965). IR intensity measurements; includes Group VIB carbonyl and nitrosyl derivatives.
344. Beck, W., Melinkoff, A., and Stahl, R., *Angew. Chem. Intern. Ed. Engl.* **4,** 692 (1965). OC—M—CO bond angles in (benzene)$Cr(CO)_3$ from IR intensity measurements.
345. Behrens, H., Mayer, K., and Müller, A., *Z. Naturforsch.* **20b,** 74 (1965). Preparation of $Cr(dipy)_3$, $Cr(phen)_3$, and $Cr(tripy)_2$ from (benzene)$Cr(CO)_3$.
346. Bennett, M. A., Interante, L. V., and Nyholm, R. S., *Z. Naturforsch.* **20b,** 633 (1965). (*o*-Allylphenyldiphenylphosphine)$M(CO)_4$.
347. Birch, A. J., Cross, P. E., and Fitton, H., *Chem. Commun.* p. 366 (1965). Reaction of $M(CO)_6$ with 1-methoxycyclohexa-1,4-diene and related compounds to give π-arene metal tricarbonyls.
348. Brown, D. A., and Carroll, D. G., *J. Chem. Soc.* p. 2822 (1965). Far infrared spectra of $ArCr(CO)_3$ complexes.
349. Bullen, G. J., *Acta Cryst.* **18,** 974 (1965). Crystallographic data for (diars)$M(CO)_4$.
350. Chandrasegaran, L., and Rodley, G. A., *Inorg. Chem.* **4,** 1360 (1965). Tertiary phosphine and arsine oxide derivatives of $Mo(CO)_6$ and $W(CO)_6$.
351. Cook, C. D., Nyholm, R. S., and Tobe, M. L., *J. Chem. Soc.* p. 4194 (1965). Tritertiary arsine tricarbonyl complexes and their halogenic derivatives.
352. Cotton, F. A., and Wing, R. M., *Inorg. Chem.* **4,** 314 (1965). Crystal and molecular structure of (dien)$Mo(CO)_3$. Dependence of Mo—C bond length upon bond order.
353. Drefahl, G., Hörhold, H., and Kuhne, K., *Chem. Ber.* **98,** 2248 (1965). Preparation of (π-styryl)$Cr(CO)_3$ complexes through the Wittig reaction.
354. Dobard, R., Fournari, P., and Besançon, J., *Compt. Rend.* **260,** 2833 (1965). Polarographic investigation of the structure of (benzylphenyl ketone)$Cr(CO)_3$.
355. Fischer, E. O., and Kohl, E. J., *Chem. Ber.* **98,** 2134 (1965). Cp(1,3-cyclohexadiene)W(CO)H.

---

* These papers are not explicitly mentioned in text or tables.

356. Fowles, G. W. A., and Jenkins, D. K., *Chem. Commun.* p. 61 (1965). Phosphoro- and arsinobenzene derivatives of $M(CO)_6$.
357. Ganorkar, M. C., and Stiddard, M. H. B., *J. Chem. Soc.* p. 3494 (1965). Heptacoordinate halogenocarbonyl anions of Mo(II) and W(II).
358. Ganorkar, M. C., and Stiddard, M. H. B., *J. Chem. Soc.* p. 5346 (1965). Substituted Group VIB carbonyl derivatives containing 2,6-dimethylpyrazine and tripy.
359. Holmes, J. D., Jones, D. A. K., and Pettit, R., *J. Organometal. Chem.* **4,** 324 (1965). Electronic effects in Group VIB arene metal carbonyl complexes and related species.
360. King, R. B., and Bisnette, M. B., *Inorg. Chem.* **4,** 475 (1965). Reactions of ions prepared from $[(indenyl)Mo(CO)_3]_2$ and $(azulene)Mo_2(CO)_6$.
361. King, R. B., and Bisnette, M. B., *Inorg. Chem.* **4,** 486 (1965). Reactions of chloroalkyl sulfides with Cp metal carbonyl anions.
362. King, R. B., Bisnette, M. B., and Fronzaglia, A., *J. Organometal. Chem.* **4,** 256 (1965). Methoxycarbonyl derivatives of Cp metal carbonyls.
363. Lauterbur, P. C., and King, R. B., *J. Am. Chem. Soc.* **87,** 3266 (1965). C^{13} NMR of Cp and olefinic derivatives.
364. Lewis, J., and Whyman, R., *J. Chem. Soc.* p. 5486 (1965). Action of halogens on diphosphine Mo and W carbonyls.
365. McFarlane, H. C. E., and McFarlane, W., *J. Inorg. Nucl. Chem.* **27,** 1059 (1965). Binuclear 1,4-dithian derivatives of $Mo(CO)_6$ and $W(CO)_6$ and an iodination product.
366. Manuel, T. A., *Advan. Organometal. Chem.* **3,** 181 (1965). Review: Lewis base metal carbonyl complexes.
367. Murdoch, H. D., *J. Organometal. Chem.* **4,** 119 (1965). π-Allyl complexes of the type $[Et_4N]^+[M_2X_3(C_3H_5)_2(CO)_4]^-$ (M = Mo, W; X = halogen).
368. Nesmayanov, A. N., Anisimov, K. N., Kolobova, N. E., and Zakharova, M. J., *Izvest. Akad. Nauk SSSR, Ser. Khim.* p. 1122 (1965). Polymetallic compounds of Sn with metal carbonyls.
369. Schmutzler, R., *Chem. Ber.* **98,** 552 (1965). Preparation of $(\phi PF_2)_3Mo(CO)_3$.
370. Strohmeier, W., and Hellmann, H., *Ber. Bunsenges. Physik. Chem.* **69,** 178 (1965). Partial bond moments of $ArM(CO)_2$(alkene) and $ArM(CO)_2$(alkyne) derivatives.
371. Strohmeier, W., and Hellmann, H., *Chem. Ber.* **98,** 1598 (1965). $ArCr(CO)_2$-(olefin) and $ArCr(CO)_2$(acetylene) derivatives.
372. Strohmeier, W., Guttenberger, J. F., and Popp, G., *Chem. Ber.* **98,** 2248 (1965). $M(CO)_5D$ complexes of S-bonded ligands and assessment of their relative σ-donating and π-accepting abilities.
373. Tate, D. P., Buss, A. A., Augl, J. M., Ross, B. L., Grasselli, J. G., Ritchey, W. M., and Knoll, F. J., *Inorg. Chem.* **4,** 1323 (1965). $Bis(acrolein)Mo(CO)_2$.
374. Thompson, D. T., *J. Organometal. Chem.* **4,** 74 (1965). P and As bridged carbonyl complexes of Mo.
375. Verkade, J. G., McCarley, R. E., Hendricker, D. G., and King, R. W., *Inorg. Chem.* **4,** 228 (1965). Derivatives of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.
376. Willeford, Jr., B. R., and Fischer, E. O., *J. Organometal. Chem.* **4,** 109 (1965). $(Anthracene)Cr(CO)_3$.
377. Winstein, S., Kaesz, H. D., Kreiter, C. G., and Friedrich, E. C., *J. Am. Chem. Soc.* **87,** 3267 (1965). (π-cyclooctatetraene)$Mo(CO)_3$ and its protonation product, (homotropylium)$Mo(CO)_3^+$.

ADDITIONAL SUPPLEMENTARY REFERENCES*

378. Angelici, R. J., and Graham, J. R., *J. Am. Chem. Soc.* **87,** 5586 (1965). Kinetics of reaction of $Cr(CO)_4(dipy)$ with phosphites to form mixed complexes of the type $M(CO)_3XY$.

379. Blaikie, P. E., Mills, O. S., Pauson, P. L., Smith, G. A., and Valentine, J., *Chem. Commun.* p. 425 (1965). X-ray study of (cycloheptatriene)$Cr(CO)_3$.

380. Bradley, D. C., Charalambous, J., and Jain, S., *Chem. Ind. (London)* p. 1730 (1965). Adducts of the type, $M'(MNe_2)_4{\cdot}2Mo(CO)_6$; $M' = Zr, Hf$.

381. Buczkowski, Z., *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **13,** 531 (1965). Proton NMR spectra of (stilbene)$Cr(CO)_3$ complexes.

382. Clark, R. J., and Hoberman, P. I., *Inorg. Chem.* **4,** 1771 (1965). $(PF_3)_xMo(CO)_{6-x}$ complexes ($x = 1 - 6$).

383. Fischer, E. O., and Ruehle, H., *Z. Anorg. Allgem. Chem.* **341,** 137 (1965). Reactions of N-carboxyazepines with metal hexacarbonyls.

384. Graham, J. R., and Angelici, R. J., *J. Am. Chem. Soc.* **87,** 5590 (1965). Kinetics of reactions of $Mo(CO)_4(dipy)$ and $W(CO)_4(dipy)$ with phosphites.

385. Handy, L. B., Treichel, P. M., Dahl, L. F., and Hayter, R. G., *J. Am. Chem. Soc.* **88,** 366 (1966). Structure and bonding in $HCr_2(CO)_{10}^-$. First known linear electron deficient X–H–X molecular system stabilized by a three-center, one electron pair bond.

386. Johnson, M. P., and Schriver, D. F., *J. Am. Chem. Soc.* **88,** 301 (1966). $CpMo(CO)_3^-$ and $CpW(CO)_3^-$ fail to add BF_3.

387. King, R. B., and Bisnette, M. B., *Inorg. Chem.* **5,** 293 (1966). Cyclic acyl derivatives from haloalkyl amines and Mo and W carbonyl anions.

388. King, R. B., and Bisnette, M. B., *Inorg. Chem.* **5,** 300 (1966). Arylazo derivatives of $CpMo(CO)_3^-$ and their substitution products containing phosphorus and sulfur-bonded ligands.

389. King, R. B., and Bisnette, M. B., *Inorg. Chem.* **5,** 306 (1966). Reaction of $CpMo(CO)_3^-$ with chloromethyl isocyanate.

390. King, R. B., and Fronzaglia, A., *Chem. Commun.* p. 547 (1965). Polyolefinic substitution products of $W(CO)_3(NCCH_3)_3$.

391. Leigh, G. J., and Fischer, E. O., *J. Organometal. Chem.* **4,** 461 (1965). Reactions of 1,3- and 1,3-cyclooctadiene with $M(CO)_6$.

392. Lewis, J., and Whyman, R., *Chem. Commun.* p. 159 (1965). Mo(I) and W(I) dicarbonyl complexes containing $C_2H_4(P\phi_2)_2$.

393. Nyholm, R. S., Snow, M. R., and Stiddard, M. H. B., *J. Chem. Soc.* p. 6564 (1965). Aliphatic tritertiary arsine complexes of Group VIB metal carbonyls.

394. Nyholm, R. S., Snow, M. R., and Stiddard, M. H. B., *J. Chem. Soc.* p. 6570 (1965). Halogenic oxidation of tritertiary arsine derivatives of Group VIB metal carbonyls.

395. Poilblanc, R., and Bigorgne, M., *J. Organometal. Chem.* **5,** 93 (1966). Assignments of CO stretching vibration bands in metal hexacarbonyl derivatives.

396. Snow, M. R., and Stiddard, M. H. B., *Chem. Commun.* p. 580A (1965). (Hexamethylbenzene)$W(CO)_3Cl^+$.

397. Werner, H., *J. Organometal. Chem.* **5,** 79 (1966). Mechanism of the substitution in $Mo(CO)_6$ with amines and phosphines.

398. Werner, H., and Prinz, R., *J. Organometal. Chem.* **5,** 79 (1966). Reaction kinetics of $Mo(CO)_6$ with aromatic and olefinic π-donors.

* These papers are not explicitly mentioned in text or tables.