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Review

THE REACTIVITY PATTERNS OF METAL CARBONYL ANIONS AND THEIR DERIVATIVES

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Contents

Abbreviations

acac = acetylacetonate
Ar = aryl
bipy = α,α'-bipyridyl
C_5H_5 = cyclopentadienyl
diars = *ortho*-phenylenebis(dimethylarsine)
diglyme = diethyleneglycol dimethyl ether
DME = dimethoxyethane
dmpe = 1,2 bis(dimethylphosphino)ethane
DMSO = dimethyl sulfoxide
dppe = 1,2 bis(diphenylphosphino)ethane
en = ethylenediamine
HMPA = hexamethylphosphoramide
o-phen = *ortho*-phenanthroline
o-triars = bis(*o*-dimethylarsinophenyl)methylarsine
py = pyridine
R = alkyl and, where noted, aryl
THF = tetrahydrofuran

I. Introduction

The chemistry of the carbonylmetallate anions and other coordinatively saturated anionic species containing transition metals in low formal oxidation states has been the subject of intense interest and effort over the past decade [1]. Thus far, only mononuclear carbonylmetallate mono- and di-anions have been reported; however, derivatives of presently unknown monouclear trianions have been prepared (see later).

Although the chemistry of these anions is very diverse, it is possible because of the strong tendency for the metals in these compounds to achieve a closed shell configuration to make very convincing analogies between the reactivity patterns of these species and those of corresponding non-metallic main group compounds in which there is a similar tendency for the constituent elements to achieve a closed shell configuration. Thus, it has become apparent to workers in organotransition metal chemistry that the 18-electron rule, when applied with discretion [2], is as important in predicting and rationalizing the stoichiometry, structure and reactivity patterns of transition

TABLE 1

ELECTRONICALLY EQUIVALENT MAIN GROUP AND TRANSITION METAL SPECIES

Main group atom and transition metal analogue	Electrons needed for closed shell configuration	Corresponding anionic forms
I and $Co(CO)_4$	1	I^- and $Co(CO)_4^-$
S and $Fe(CO)_4$	2	S^{2-} and $Fe(CO)_4^{2-}$
P and $Co(CO)_3$	3	P^{3-} and $[Co(CO)_3^{3-}]^a$

[a] Presently known only in the form of derivatives.

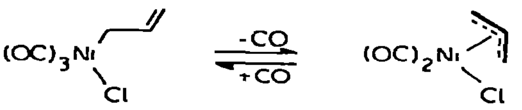
metal compounds containing CO, PF_3 and other π-acceptor ligands [3] as the octet rule is for compounds containing only first row non-metals. For example, the reactivity patterns of neutral 18-, 17- and 16-electron metal species have been found to closely resemble those of saturated, free radical and carbene organic groups, respectively. Similarly, it has been noted that the carbonylmetallate monoanions act like carbanions [4]. However, as will be shown below, these monoanions behave more like halides and pseudohalides than carbanions. Moreover, the parallels in the chemistry of the carbonyl anions and halides and, especially, pseudohalides are sufficiently far reaching that it is useful to classify the former as transition metal pseudohalides. This resemblance has been noted by Jorgensen in a brief account of the chemistry of metal carbonyls [5]. In analogous fashion, evidence that the carbonylmetallate dianions and presently unknown trianions may be classified as transition metal pseudochalcogenides and pseudopnicogenides will be presented. The latter terms apparently have not been used previously and are derived from chalcogen [6] and pnicogen [7], which are group names for the VIa and Va family of elements, respectively. Representative members of electronically equivalent main group and transition metal species are shown in Table 1. These species are said to be electronically equivalent in that each requires the same number of electrons to attain a closed-shell configuration. The above relationships are quite useful in rationalizing known and predicting new reactivity patterns of electronically equivalent main group and transition metal species; however, it is important to recognize that there are limitations in this scheme as follows:

1. Metal carbonyl groups and other organotransition metallic units undergo a variety of reactions which are usually less facile or in some cases unprecedented in main group chemistry. Such reactions are extremely important in the ability of these species to function as effective stoichiometric and catalytic reagents in organic synthesis. The most important of these are:

a. Formation of coordinatively unsaturated or carbenoid species, e.g.,

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO$$

b. Intramolecular substitution (σ—π equilibrium)



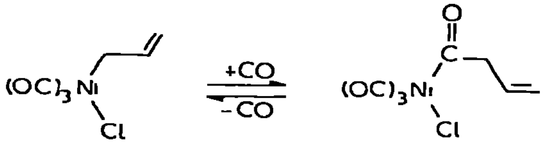
σ-allyl π-allyl

c. Formation of cluster compounds

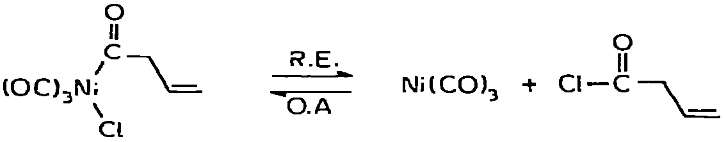
$C_6H_5Ge[Co(CO)_4] \xrightarrow{\Delta} C_6H_5Ge[Co(CO)_3]_3 + 3CO$

an uncondensed species   a metal cluster

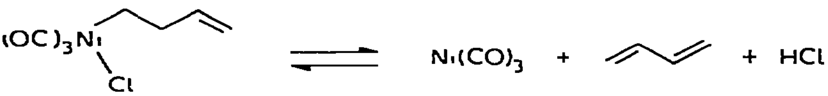
d. Alkyl migration (CO insertion)



e. Reductive elimination (reverse step is oxidative addition)

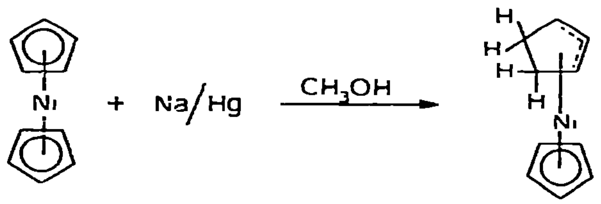


f. β-Elimination



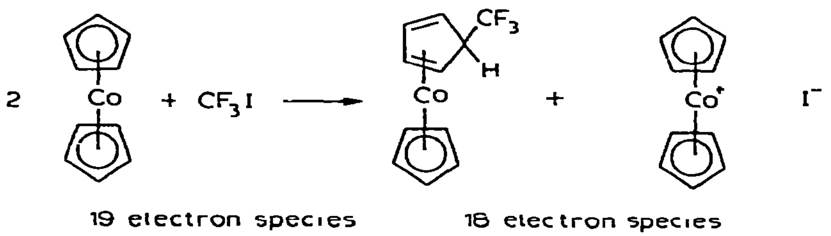
The relative ease with which neutral metal carbonyl units lose carbon monoxide groups accounts for the importance of steps a, b, c and the reverse of d. Steps e and f have been observed with main group compounds, but generally these processes are more facile for transition metal species. A monograph has been published recently which discusses these and related reactions in detail [398].

2. Organotransition metal species, with very few exceptions, do not undergo valence shell expansion (e.g., 18→20 electrons) or exist as stable entities with the transition metal having more electrons than it requires to attain a closed shell configuration [3]. Nickelocene and cobaltocene are two important apparent exceptions to this rule. They are both exceedingly reactive species and tend to form products in which the metals attain the preferred closed shell configuration, e.g.,



[333]

20 electron species   18 electron species



[309]

In contrast, numerous second and higher row main group non-metals often undergo valence shell expansions in reactions, e.g., $PCl_3 + Cl_2 \rightarrow PCl_5$. As a result there are numerous main group compounds such as SbF_6^-, SCl_4 and IF_3 which have no counterpart in organotransition metal chemistry. This observation serves to emphasize the importance of the 18-electron rule in rationalizing the stoichiometry of all coordinatively saturated organotransition metal species.

Except for these limitations, however important, mononuclear metal carbonyl units which lack 1,2 and 3 electrons in achieving a closed shell configuration may profitably be considered as large and polarizable pseudohalogens, pseudochalcogens and pseudopnicogens, respectively.

The experimental basis for these analogies will now be assessed by grouping the principal reactivity patterns of the anions to emphasize their close formal relationship with the halides (and main group pseudohalides), chalcogenides and pnicogenides and derivatives thereof, respectively. In this manner it is hoped to achieve a reasonably coherent approach to the chemistry of the carbonylmetallate anions and related species.

II. Carbonyl monoanions

These have been studied extensively and reliable procedures for their preparation [8], including a very efficient NaK alloy reduction method [9], have been developed. Their chemical properties are generally well established; they react with appropriate substrates to form the following classes of compounds:

A. Covalent adducts, usually with soft bases.

B. Hydrides, HX, which range from very strong to exceedingly weak protonic acids.

C. Neutral and charged interhalogenoid compounds.

D. Dimeric neutral metal carbonyls or in rare instances monomeric radicals.

E. Adducts with unsaturated species.

These reactivity patterns are diagnostic of pseudohalides [10-13c] and will now be discussed in detail.

A. Covalent adducts

1. Adducts containing Main Group and Group 1B transitional elements

a. Neutral compounds

The monoanions generally behave as soft and thus strongly nucleophilic Lewis bases [14]. Consequently, soft metal cations interact with many of them and/or their conjugate acid to form compounds which are but sparingly soluble in water. Typical examples are:

$2NaMn(CO)_5 + Hg(CN)_2 \rightarrow Hg[Mn(CO)_5]_2 + 2NaCN$ [15]

$HCo(CO)_3PPh_3 + TlNO_3 \rightarrow TlCo(CO)_3PPh_3 + HNO_3$ [16]

$NaCo(CO)_4 + AgNO_3 \rightarrow AgCo(CO)_4 + NaNO_3$ [17]

In addition, a vast number of other covalent adducts containing substituted main group metals and non-metals have been prepared, in most instances by treating an appropriate halide with a monoanion [1]. Representative examples include $CH_3Mn(CO)_5$ [18], $Zn[Co(CO)_4]_2$ [19], and $Ph_3SnV(CO)_6$ [20]. Those adducts that are bound to weakly basic carbonylmetallate anions readily undergo heterolytic cleavage in the presence of competing bases, e.g., solvent [21] or soluble halide [22]. For example, a particularly base-sensitive species, $Ph_3SnV(CO)_6$, is completely dissociated to solvated Ph_3Sn^+ and $V(CO)_6^-$ in tetrahydrofuran. In methylene chloride the Sn—V bond is instantly cleaved by an equivalent of Et_4NCl to give Ph_3SnCl and the salt $[Et_4N][V(CO)_6]$ [23]. Analogous ionizations or solvolyses of corresponding halide and main group pseudohalide species have been recognized for many years [24]. Organosilicon halides and pseudohalides are particularly sensitive to solvolysis in polar solvents. Corresponding metal carbonyl derivatives, such as $Me_3SiMn(CO)_5$ [25] and $Me_3SiCo(CO)_4$ [24,27] are similarly solvent-sensitive. Consequently, they generally cannot be prepared in tetrahydrofuran or solvents of greater donor strength [1, 24]. Related ligand exchange or redistribution reactions have also been observed as shown by the following equations:

$Ph_3SnV(CO)_6 + Ph_3PAuCl \rightarrow Ph_3PAuV(CO)_6 + Ph_3SnCl$ [28]

$HgI_2 + Hg[Mo(CO)_3C_5H_5]_2 \rightarrow 2IHgMo(CO)_3C_5H_5$ [28]

$2[C_5H_5(CO)_2Fe]Cd[Co(CO)_4] \rightleftharpoons Cd[Fe(CO)_2C_5H_5]_2 + Cd[Co(CO)_4]_2$ [19]

$2[C_5H_5(CO)_2PPh_3Mo]SnMe_3 \rightarrow Me_4Sn + [C_5H_5(CO)_2PPh_3Mo]_2SnMe_2$ [29]

Such reactions are well known for main group species [30] including organometallic pseudohalides [13b] but only recently has this reactivity pattern been recognized as an important one for metal carbonyl derivatives [30a].

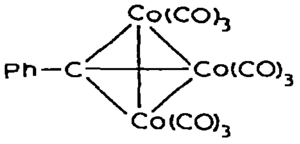
b. Ionic compounds

Carbonylmetallate anions also form charged complexes with main group metals, metalloids and Group 1B transition metals; e.g., $Ag[Mo(CO)_3C_5H_5]_2^-$ [31], $Cl_2Sb[Fe(CO)_2C_5H_5]_2^+$ [32], $Hg[Co(CO)_4]_3^-$ [33], $In[Co(CO)_4]_4^-$ [33], $Br_3GaCo(CO)_4^-$ [34], and $H_3BRe(CO)_5^-$ [35]. Analogous halide and main group pseudohalide containing complexes have been known for many years, e.g., $Ag(NCO)_2^-$ [36], $AsCl_4^+$ [37], $Hg(SCN)_3^-$ [38], $InBr_4^-$ [39, 40], $Ga(NCS)_4^-$ [41] and H_3BCN^- [42]. The methods used to prepare both the main group and transition metal compounds are very similar.

c. Condensation reactions: formation of transition metal cluster compounds

For several years it has been known that whenever more than one metal carbonyl group is coordinated to a single atom, intramolecular displacement of one or more carbon monoxide molecules with concomitant formation of metal—

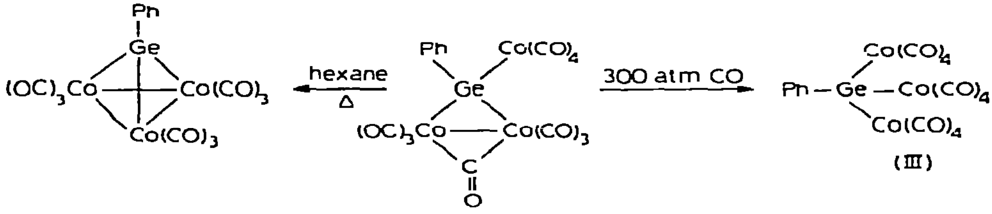
metal bonds can occur. Although, in principle, any metal carbonyl moiety could undergo such a condensation reaction, $Co(CO)_4$ groups seem particularly susceptible to this mode of interaction which has no precedent in the chemistry of main group pseudohalides. One classic example involves the reaction of α,α,α-trichlorotoluene with three equivalents of $Co(CO)_4^-$ to give $C_6H_5CCo_3(CO)_9$ (I) instead of the anticipated uncondensed $C_6H_5C[Co(CO)_4]_3$ [43].



(I)

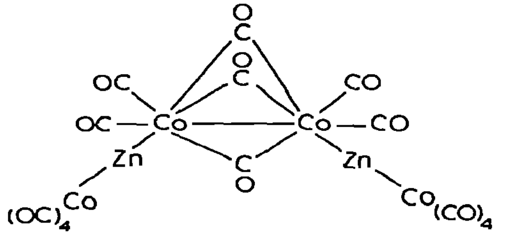
The nature of the main group atom is important. For example, although the germanium analogue of (I), $PhGeCo_3(CO)_9$, can be prepared by refluxing the partially condensed $PhGeCo_3(CO)_{11}$ (II) in hexane, the corresponding silicon derivative, $PhSiCo_3(CO)_9$, is unknown and apparently cannot be prepared from the known $PhSiCo_3(CO)_{11}$ [44].

It is interesting to note that under high pressures of CO, II is converted to the thermally unstable $PhGe[Co(CO)_4]_3$ (III). The tin analogue, $PhSn[Co(CO)_4]_3$ has been prepared, but attempts to convert it to either $PhSnCo_3(CO)_{11}$ or $PhSn$-$Co_3(CO)_9$ have failed [45].



(II) (III) [44]

Another recently reported condensation reaction involves the formation of $Zn_2Co_4(CO)_{15}$, postulated to have the structure IV, from $Zn[Co(CO)_4]_2$ under a variety of conditions [46].



(IV)

The structure can be considered to be derived from that of $Fe_2(CO)_9$ [47], with two one electron donor $ZnCo(CO)_4$ units replacing two terminal carbonyl groups. Similar condensed species such as $AsCo_3(CO)_9$, $As_3Co(CO)_3$, $P_2[Co$-$(CO)_3]_2$ etc. will be discussed under transition metal pseudopnicogen chemistry. Metal carbonyl anions also interact with certain transition metal cations to form metal cluster compounds. These will be discussed in section A3.

2. *Isocarbonyls and related species*

The vast majority of electrophiles, E^+, react with metal carbonyl anions to form adducts which contain a direct E—M bond, where M is the transition metal in the carbonyl anion. However, in recent years it has been shown that certain electrophiles, particularly those containing Mg, B, Al, Si and other atoms which strongly interact with oxygen, can react with neutral carbonyl species [48, 49] as well as carbonyl anions to form "isocarbonyls" [50], i.e., species containing an M—C—O—E linkage. Such linkages have been suggested for or observed in the following carbonyl anion derivatives: $C_5H_5W(CO)_3AlPh_3^-$ [51], $Al(C_5H_5W(CO)_3)_3(THF)_3$ [52], $[C_5H_5W(CO)_3AlMe_2]_2$ [53], $MgX_2 \cdot 4py$ (X = $C_5H_5Mo(CO)_3$, $C_5H_5Fe(CO)_2$, $Co(CO)_4$, $Mn(CO)_5$, [54], $Mn[C_5H_5Mo(CO)_3]_2 \cdot 4py$ [55], $acacHo[Mn(CO)_5]_2 \cdot 2Et_2O$ [56] and "$Co_3[Fe(CN)_5CO]_2 \cdot 5.7\ H_2O$" [57]. The latter three species are apparently the first isolated complexes to contain M—C—O—M′ linkages when both M and M′ are transition metals. Although the isocarbonyl nature of these species is postulated principally on the basis of their abnormally low carbonyl stretching frequencies, the evidence for the manganese species is particularly compelling since its infrared spectrum in the CO stretching frequency region is nearly identical with the above magnesium analogue whose structure has been established by X-ray crystallography [54].

In view of the existence of isocarbonyls the following type of equilibrium with an appropriate electrophile and carbonyl anion is possible:

$$(OC)_yM \rightarrow E \rightleftharpoons (OC)_{y-1}\overset{-}{M}{=}C{=}\overset{+}{O} \rightarrow E$$

Although such linkage isomers and equilibria are well known for heteroatomic pseudohalides, especially the thiocyanate ion [13], none have been established thus far for carbonyl anions. However, recent observations may be explained or at least rationalized on the basis of such equilibria. A particularly interesting observation concerns the reports of two nearly identical compounds, $Mg[Fe(CO)_2C_5H_5]_2 \cdot 2py$ [58] and $Mg[Fe(CO)_2C_5H_5]_2 \cdot 4py$ [54]. The former is postulated to contain direct Mg—Fe linkages on the basis of its infrared spectrum in benzene, while the latter has a much different spectrum in pyridine and, as mentioned above, is thought to contain isocarbonyl groups [54]. It is tempting to suggest that in appropriate solvents or solvent mixtures these compounds will exhibit isocarbonyl—carbonyl equilibria. Indeed, the number of carbonyl bands observed for the dipyridine adduct is in excess of that predicted on the basis of local symmetry. While this may be attributed to "vibrational coupling across the Fe—Mg—Fe linkage" [58], an isocarbonyl—carbonyl equilibrium may also be partially or wholly responsible. Since such vibrational coupling should be largely independent of concentration effects, a concentration dependence study of the infrared spectrum in the carbonyl region could clarify the situation.

The presence of isocarbonyl intermediates may also be implicated in the observed stereochemical nonrigidity and *cis—trans* isomerizations of silylruthenium and silylosmium tetracarbonyls. However, the authors' suggestion that these possibly arise via an acyl intermediate seems more plausible in view of the observed stereochemical non-rigidity of similar stannyl derivatives [59] since there have been no reports of species containing Sn—O—C—M linkages.

However, such isomerizations are possible at least in other organosilyl species. This is evident from the recent report that the trimethylsilyl group in $Me_3Si{-}Co(CO)_4$, which undoubtedly contains a Si—Co bond [60], "migrates" from Co to a carbonyl oxygen when heated in the absence of solvent. Although the reaction does not give rise to an isolable isomeric species, one of the products has been identified as $Me_3SiOCCo_3(CO)_9$ [61], which contains a Co—C—O—Si linkage [62]. The latter species is also obtained in high yield by either treating $Me_3SiCo(CO)_4$ with tetrahydrofuran (THF) [61] or by treating the alkoxycarbonyl anion, $^-OCCo_3(CO)_9$ with Me_3SiCl [62]. The solvolytic instability of organosilyl derivatives of carbonyl monoanions was mentioned previously in this paper and is emphasized by the above example as well as a related report on attempted preparations of triphenylsilyl derivatives of metal carbonyl anions [63].

It is also appropriate here to point out that diamagnetic cyanide substituted carbonyl anions react with electrophilic species to give only isocyanide derivatives. Thus, at least in cases studied so far, the nitrogen of the cyanide is a stronger Lewis base than either the metal center or the oxygen of the carbonyl. Examples of such isocyanide metal carbonyls are: $LNCMo(CO)_5$ (L = H, Me_3Si, Me_3Sn [64]), $LNCFe(CO)_4$ (L = Me_3Si, Me_3Ge [65], CH_3, C_6H_5 [66]), $[(OC)_4Fe{-}N{-}CFe(CO)_4]^-$ and $[(OC)_5CrCNCr(CO)_5]^-$ [67].

Similar reactions of other coordinated cyanides have been recognized for many years [68]. In contrast, the pentacyanocobaltate(II) anion, a paramagnetic species, undergoes a distinctly different reaction with electrophilic species such as CH_3I giving rise to an equimolar mixture of $[H_3CCo(CN)_5]^{3-}$ and $[ICo(CN)_5]^{3-}$, where the substituents are all bonded to the cobalt center. Such reactivity patterns can be readily understood on the basis of the 17 electron coordinatively unsaturated nature of this and similar species [69].

3. Adducts containing d- and f- block transition metals

a. Uncondensed products

Recently, carbonylmetallate monoanions have also been used as ligands to form coordination compounds of transition metals. Examples are: $(Ph_3P)_2Ni[Co(CO)_3X]_2$ (X = CO, Ph_3P [69a]), *trans*-py_2ML_2 (M = Pd, Pt; L = $Mn(CO)_5$, $Co(CO)_4$, $C_5H_5Mo(CO)_3$ [70, 71]), *trans*-$py_2Pt[C_5H_5Mo(CO)_3]Cl$ [70, 71], $PtCl[Fe(CO)_2{-}\pi{-}C_5H_5](PPh_3)_2$ [72], $[\{(NC)_2C_2S_2\}Mn(CO)_5\}]^{2-}$ (M = Co, Fe) [73], $U[Mn(CO)_5]_4$ [74], $Er[Co(CO)_4]_3 \cdot 4THF$ [75], $Mn[C_5H_5Mo(CO)_3]_2 \cdot 4py$ [55], $acacHo[Mn(CO)_5]_2 \cdot 2Et_2O$ [56] and $Co_3[Fe(CN)_5CO]_2 \cdot 5.7\ H_2O$ [57]. All of these species except the last three are believed to contain metal—metal bonds.

The uranium and erbium species are noteworthy in that they are postulated to be the first *f*-block compounds ever isolated which contain metal—metal bonds. The last three were mentioned in section A2 and are considered to contain isocarbonyl linkages. In all cases, except possibly the maleonitriledithiolate complexes, formally analogous compounds have been prepared with main group pseudohalides. Very little work has been reported in this potentially fruitful field. In addition to the above complexes, a large variety of Group

Ib species containing metal—metal bonds have been prepared [76]. Several of these were described in section A1.

b. Condensed products: metal cluster compounds

For several years it has been known that the interaction of Co^{II} salts and $Co(CO)_4^-$ in ethanol can give rise to the cobalt cluster anion $Co_6(CO)_{15}^{2-}$. Possibly a cobalt(II) adduct containing two $Co(CO)_4^-$ units initially forms $[Co_3(CO)_8]$, a paramagnetic species, which eventually yields the observed hexanuclear cobalt dianion [77]. Mixed Ni—Co cluster anions, $NiCo_3(CO)_{11}^-$ and $Ni_2Co_4(CO)_{14}^{2-}$, have also been reported recently and are formed by the interaction of simple Ni^{II} salts with varying amounts of $Co(CO)_4^-$ [78a]. Such interactions of *d*-block transition metal cations with carbonyl anions are possible whenever the cations can be reduced by the anions. Since many of the latter are potent reducing agents, there would appear to be numerous combinations that could form new clusters. However, in some cases trivial reactions occur. For example, it is known that $C_5H_5Fe(CO)_2^-$ is rapidly and quantitatively oxidized to $[C_5H_5Fe(CO)_2]_2$ by $CrCl_3 \cdot 3THF$ in tetrahydrofuran [78]. This reaction is reminiscent of the quantitative oxidation of I^- to I_2 by aqueous solutions of Fe^{III}.

Another type of condensation reaction is exemplified by the formation of the previously mentioned $^-OCCo_3(CO)_9$ (Section 2) from the reduction of $Co_2(CO)_8$ by solid sodium metal in THF [62]. The product probably results from the condensation of an intermediate such as $[\{(OC)_4Co\}_2Co(CO)_3]^-$ which could form in an initial nucleophilic attack of $Co(CO)_4^-$ on $Co_2(CO)_8$. Such attacks of carbonyl anions on mononuclear neutral carbonyls are well established, e.g.,

$Co(CO)_4^- + Fe(CO)_5 \rightarrow [FeCo(CO)_8]^-$ [79]

It is clear that much work remains to be done particularly where the electrophilic species is a transition metal species in a "normal" (II, III) or "high" (> III) formal oxidation state. The development of general methods for the preparation of new metal atom clusters which may be useful as either homogeneous or heterogeneous catalysts is an anticipated fruit of such investigations.

B. Hydrides

On protonation, carbonylmetallate anions generally yield hydroacids or metal hydrides (recent reviews: refs. 48, 80-87) which are often volatile and/or unstable substances with respect to decomposition to hydrogen and neutral dimeric species. For example, treatment of $NaCo(CO)_4$ with H_3PO_4 yields volatile, oxygen sensitive, $HCo(CO)_4$, which slowly decomposes as a liquid at —20° to hydrogen and $Co_2(CO)_8$ [88]. The latter reaction can be reversed under high pressures of hydrogen (and free CO to prevent formation of condensed Co carbonyls [89]) to give good yields of the hydride [90]. In aqueous solution $HCo(CO)_4$ is completely dissociated [91]. The infrared [92] and proton NMR [93] spectra of $HCo(CO)_4$ are consistent with a trigonal bipyramidal molecule in which the hydride is directly bonded to the cobalt and

TABLE 2

A COMPARISON OF SELECTED PROPERTIES OF $HCo(CO)_4$ AND HI

	$HCo(CO)_4$	HI
1. Thermal decomposition	H_2 + $Co_2(CO)_8$, slowly at −20° [88]	H_2 + I_2, slowly at 100°C [95]
2. Percent dissociation of HX in dilute aqueous solutions	∿ 100% [91]	∿ 100% [94]
3. Reaction with aqueous $AgNO_3$	$AgCo(CO)_4$ [17] precipitate	AgI (94) precipitate [94]
4. Reaction with O_2	H_2O + $Co_2(CO)_8$ [96][a]	H_2O + I_2 [94]
5. Reaction with CH_3MgBr	CH_4 + $MgBrCo(CO)_4$ [97]	CH_4 + MgBrI [94]

[a] An excess of O_2 decomposes the $Co_2(CO_8)$.

occupies the axial site. It is interesting to note that no isocarbonyl hydrides have been characterized. However, it seems possible that $HV(CO)_6$ in non-polar media may be such a species in view of the demonstrated reluctance of $V(CO)_6^-$ to form seven coordinate adducts [23]. From the above information and that in Table 2 it is evident that the chemical properties of $HCo(CO)_4$ are not unlike those of HI ([94], see Table 1), which is in accord with the suggested pseudohalide character of $Co(CO)_4^-$.

A few other neutral carbonyl hydride species are also strong acids; e.g., $HV(CO)_6$ (free acid is unknown) [98] and $HCo(CO)(PF_3)_3$ [99]. However, most others, e.g., $HCo(CO)_3PPh_3$, $HMn(CO)_5$, and $HFe(CO)_2C_5H_5$, are only slightly dissociated in water and/or alcohols [100], as are many of the hydroacids of main group pseudohalides [101]. There also exist a series of metal carbonyl hydride anions, HL_2^- (L = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$), which are structurally similar to the bihalides HX_2^- (X = F, Cl, Br, I) in that they both possess a linear L—H—L or X—H—X grouping, respectively [102]. However, the former are best regarded as monoprotonated derivatives of $M_2(CO)_{10}^{2-}$ (M = Cr, Mo, W), which do not behave as pseudohalides (Part III).

C. Neutral and charged interhalogenoid compounds

Interhalogenoid compounds such as $(OC)_5ReCo(CO)_4$ [103], $IMn(CO)_5$ [104], $C_5H_5Fe(CO)_2NCSe$ [105], etc., can generally be prepared in the same fashion as are interhalogens; e.g.,

$[Mn(CO)_5]_2 + [Re(CO)_5]_2 \rightarrow 2(OC)_5Re{-}Mn(CO)_5$ [106]

$[Mn(CO)_5]_2 + (SCN)_2 \rightarrow 2NCSMn(CO)_5$ [107]

$[C_5H_5Fe(CO)_2]_2 + MeSSMe \rightarrow 2MeSFe(CO)_2C_5H_5$ [108]

$2V(CO)_4(Ph_2PCH_2CH_2PPh_2) + I_2 \rightarrow 2IV(CO)_4(Ph_2PCH_2CH_2PPh_2)$ [109]

Many are also available by nucleophilic substitutions; e.g.,

$Mn(CO)_5^- + BrRe(CO)_5 \rightarrow (OC)_5Re{-}Mn(CO)_5$ [110]

$Mn(CO)_5^- + ClSCN \rightarrow NCSMn(CO)_5$ [111]

In certain cases transition metal interhalogenoids have been made by the action of Ag^I or Tl^I salts on appropriate substrates. Examples are as follows:

$AgC(CN)_3 + C_5H_5(CO)_2FeI \rightarrow C_5H_5(CO)_2FeC(CN)_3 + AgI$ [112]

$TlCo(CO)_4 + BrMn(CO)_5 \rightarrow (OC)_5Mn{-}Co(CO)_4 + TlBr$ [113]

Under certain conditions the Tl^I may be oxidized by metal carbonyls to Tl^{III}, hence the above reaction is not of general utility [114, 115]. The silver(I) metathesis method has been used for many years as a general route to main group mixed interhalogenoids [94].

The interaction of metal carbonyl cations with Lewis bases has also been shown to give transition metal interhalogenoids:

$Re(CO)_6^+ + N_3^- \rightarrow Re(CO)_5NCO + N_2$ [116]

$C_5H_5Fe(CO)_3^+ + N_2H_4 \rightarrow C_5H_5Fe(CO)_2NCO + NH_4^+$ [117]

$C_5H_5Fe(CO)_2CS^+ + N_2H_4 \rightarrow C_5H_5Fe(CO)_2NCS + NH_4^+$ [118]

$[Re(CO)_6][Co(CO)_4] \xrightarrow{60^\circ} (OC)_5ReCo(CO)_4 + CO$ [119]

$[(Ph_3P)_2Co(CO)_3][Co(CO)_4] \xrightarrow{>40^\circ} [Ph_3PCo(CO)_3]_2 + CO$ [120]

$[V(dppe)_3][V(CO)_6]_2 \xrightarrow{120^\circ} 3V(CO)_4(dppe)$ [121]

The final two examples show how analogous cation—anion interactions can produce carbonyl dimers and, in the case of vanadium, a paramagnetic monomer.

Related halogenoid cations are also known. For example, $C_5H_5Fe(CO)_2$-$PEt_3^+\,Cl^-$ and $[C_5H_5Fe(CO)_2]_2X^+$ (X = Cl, Br, I). The former species may be regarded as a substituted phosphonium ion or a metal carbonyl cation and has been isolated (> 50% yield) from the reaction [122, 123]:

$$C_5H_5Fe(CO)_2I + PEt_3 \xrightarrow[\text{benzene}]{80^\circ} \left\{\begin{matrix} C_5H_5(CO)_2Fe{-}\overset{+}{P}Et_3 \\ \updownarrow \\ C_5H_5(CO)_2\overset{+}{Fe}{=}PEt_3 \end{matrix}\right\} I^-$$

A substituted neutral product, $C_5H_5Fe(CO)PEt_3I$, also forms (30% yield). This reaction is quite analogous to that of PMe_3 with halogens [124]; e.g., $I_2 + PMe_3 \rightarrow I\overset{+}{P}Me_3\,I^-$. With arsines and other phosphines, halogens also often yield neutral five coordinate phosphoranes [125] and arsoranes [126].

In both of these reactions the phosphorus is formally oxidized from P^{III} to P^V. Halometal carbonyls and metal carbonyl dimers can behave as oxidizing agents in the presence of appropriate substrates. This general reactivity pattern, as shown by the equation: $X_2 + N \rightarrow X{-}N{-}X$, $X{-}N^+X^-$ or $N^{2+}2X^-$, where N has an even number of electrons, is an oxidative addition reaction, one of the principal reactions of halogens or main group pseudohalogens. It will be discussed in more detail in section D with respect to the chemistry of the metal carbonyl dimers. The latter species, $[C_5H_5Fe(CO)_2]_2X^+$ (X = Cl, Br, I) is formally analogous to the halogen cations I_3^+, ICl_2^+, BrF_2^+, and ClF_2^+, [127] which may be considered to be onium ions; cf., diphenyliodonium ion, Ph_2I^+.

There appear to be no reports on the preparation of main group pseudohalide analogs of such cations; e.g., $(NCS)_2I^+$, although these would appear to be capable of existence. The first reported synthesis of the "iron halonium" ions was by the following route:

$2C_5H_5Fe(CO)_2Br + AlBr_3 \xrightarrow{SO_2(liq.)} \xrightarrow{PF_6^-} [[C_5H_5Fe(CO)_2]_2Br]PF_6$ [128]

A more recent and novel synthesis establishes that the formation of the interhalogenoid $C_5H_5Fe(CO)_2I$ from $[C_5H_5Fe(CO)_2]_2$ and I_2 in chloroform occurs via the ionic intermediate $[C_5H_5Fe(CO)_2]_2I^+X^-$ ($X = I$ or I_3) which slowly decomposes to the final product at room temperature [129]. The interaction of $[C_5H_5Ru(CO)_2]_2$ with halogens has also been studied and the salts $[C_5H_5Ru(CO)_2]_2X^+$ BPh_4^- were isolated. The chloronium and bromonium cations were unstable with respect to interaction with the BPh_4^- ion as follows:

$[C_5H_5Ru(CO)_2]_2Cl^+BPh_4^- \rightarrow C_5H_5Ru(CO)_2C_6H_5 + C_5H_5Ru(CO)_2Cl + BPh_3$ [130]

They are also very unstable to nucleophilic attack, giving rise to a mixture of interhalogenoids:

$[C_5H_5Ru(CO)_2]_2I^+ + X^- \rightarrow C_5H_5Ru(CO)_2X + C_5H_5Ru(CO)_2I$ [130]
($X = Br, Cl, N_3, SCN$)

Probably the best known class of charged triatomic halogen species are the monoanions such as I_3^-, BrI_2^-, Br_3^-, ClI_2^-, $ClBr_2^-$, etc. [131]. There also exist analogous main group halogenoid anions such as $I(SCN)_2^-$ [132], $(SeCN)_3^-$ [133], $(SeCN)I_2^-$ [133], $I_2(SCN)^-$ [133] and $I[ON(CF_3)_2]_2^-$ [134]. Presently, there are no known examples of transition metal analogues, although it seems possible that the formation of $[C_5H_5Fe(CO)_2]_2$ from $C_5H_5Fe(CO)_2I$ and $C_5H_5Fe(CO)_2^-$ could proceed via the intermediate $[C_5H_5Fe(CO)_2]_2I^-$, which would be analogous to $I(SCN)_2^-$. Perhaps a careful study of this and similar reactions at low temperatures would provide evidence for the existence of this and similar transition metal halogenoid anions. Species like $[Co(CO)_4]_3^-$ are not expected to be stable since, unlike second and higher row main group elements, transition metals in low formal oxidation states show little or no tendency to expand their coordination sphere beyond that required to formally attain the electronic configuration of the next inert gas. It has been reported that X^- ($X = Cl, Br, I$) reacts with $Mn_2(CO)_{10}$ and $XMn(CO)_5$ to give $Mn_2X_2(CO)_8^{2-}$and *cis*-$MnX_2(CO)_4^-$ [135, 136], respectively, instead of $[(OC)_5Mn]_2X^-$ and $(OC)_5MnX_2^-$, the expected products on the basis of the normal halogen or main group pseudohalogen reactivity patterns. However, the observed halocarbonyl anions result from substitution of CO by X^-. The substitution reaction is the principal reactivity pattern available to metal carbonyl anions and their derivatives for which no close correspondence in halogen or main group pseudohalogen chemistry exists.

D. Metal carbonyl dimers

Practically all carbonylmetaliate monoanions can be oxidized either electrochemically [137] or with an appropriate one electron oxidizing agent to give neutral dimeric species. These are often volatile and have chemical reactivity patterns which are strikingly similar to those of the higher halogens, particularly I_2, and the main group pseudohalogens. Some representative preparations of the dimers from carbonyl anions are represented by the following equations:

$2Mn(CO)_5^- + 2C_7H_7^+ \xrightarrow[\text{(room temp.)}]{\text{THF}} Mn_2(CO)_{10} + C_{14}H_{14}$ [138]

$2C_5H_5Fe(CO)_2^- + 2C_7H_7^+ \xrightarrow[-70^\circ]{\text{THF}} [C_5H_5Fe(CO)_2]_2 + C_{14}H_{14}$
$+ (h^5\text{-}C_5H_5)(h^1\text{-}C_7H_7)Fe(CO)_2$ (4% yield) [139]

$2V(CO)_4dppe^- + 2C_7H_7^+ \rightarrow 2V(CO)_4dppe + C_{14}H_{14}$ [109]

$2C_5H_5Cr(CO)_3^- + 2C_3H_5Cl \rightarrow 2[h^5\text{-}C_5H_5)(h^1\text{-}C_3H_5)Cr(CO)_3] \rightarrow$
(unstable)
$[C_5H_5Cr(CO)_3]_2 + C_6H_{10}$ [140]

(An atypical reaction. Generally a thermally stable σ-allyl product forms in similar reactions of allyl chloride with other carbonyl anions.)

$2V(CO)_6^- + Ph_3CCl \xrightarrow{\Delta} 2V(CO)_6 + [Ph_3C]_2 + 2Cl^-$ [141]

$C_5H_5Fe(CO)_2^- + HCl \rightarrow HFe(CO)_2C_5H_5 + Cl^- \rightarrow \frac{1}{2}[C_5H_5Fe(CO)_2]_2$ [8]
(thermally unstable)

Main group pseudohalides can also usually be oxidized to neutral dimeric pseudohalogens such as thiocyanogen, $(SCN)_2$, cyanogen, $(CN)_2$, dialkyldisulfides, $(RS)_2$, and thiuramdisulfides, $(R_2NCS_2)_2$. However, other pseudohalogens are known only in the neutral state as radicals, e.g., bis(trifluoromethyl)nitroxide, $(CF_3)_2NO$ [134], or are unknown as stable neutral entities; e.g., azide anion, N_3^-, and fulminate ion, CNO^-. Similarly, there exist a few isolable but highly reactive metal carbonyl free radicals, e.g., $V(CO)_6$ [142] and $ICr(CO)_5$ [143] as well as other species which are only known in the anionic form, e.g., $Nb(CO)_6^-$, $Ta(CO)_6^-$, $M(CO)_5PPh_3^-$ (M = V, Nb,Ta) [78]. It also appears very likely that free $Mn(CO)_5$ radicals have been generated by photochemical cleavage (λ 3500 Å) of the Mn—Mn bond in $Mn_2(CO)_{10}$ [136a].

The reactivity patterns of the metal carbonyl dimers bear a remarkably close resemblance to those of main group pseudohalogens. For example they can be:

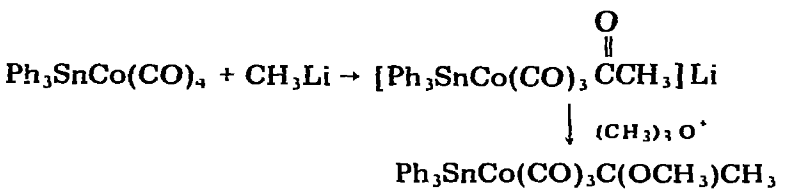
1. reduced by electropositive metals and other reducing agents to metallic salts and other metal carbonyl derivatives,
2. oxidized by halogens or halogenoids to form interhalogenoids,
3. disproportionated by suitable Lewis bases, such as the hydroxide ion,
4. treated with hydrogen to give hydroacids,
5. treated with olefins and acetylenes to give insertion products.

These five reactivity patterns will be considered below in some detail. Reactions that are also characteristic of metal carbonyl dimers but bear no obvious relationship to halogen chemistry include inter- and intra-molecular substitution reactions, the latter having been discussed in Sections A.1.c and A.3.b with respect to metal cluster formation. Examples are:

Substitution: $Mn_2(CO)_{10} + (C_6H_{11})_3P \rightarrow Mn_2(CO)_8[P(C_6H_{11})_3]_2 + 2CO$ [145]

Condensation: $2Co_2(CO)_8 \xrightarrow{\Delta} Co_4(CO)_{12} + 4CO$ [146]

Strong bases such as carbanions can also directly attack a carbonyl group giving acyl carbonyl anions which on alkylation yield carbenes [147], e.g.:



$$\mathrm{Ph_3SnCo(CO)_4 + CH_3Li \rightarrow [Ph_3SnCo(CO)_3\overset{\overset{O}{\|}}{C}CH_3]Li \xrightarrow{(CH_3)_3O^+} Ph_3SnCo(CO)_3C(OCH_3)CH_3}$$ [148]

Lewis acid attack of the oxygen in a carbonyl group has been described earlier (Section A.2). Other reactions of coordinated carbonyl groups are known [149], however, a detailed description of this very important area is beyond the scope of this paper.

Many metal carbonyl dimers can also be protonated to give species of the type HM_2^+; e.g., $[\{C_5H_5W(CO)_3\}_2H]^+PF_6^-$, $[Mn(CO)_5HFe(CO)_2C_5H_5]^+$ and $[C_5H_5Fe(CO)_2]_2H^+$ [150]. Although there are apparently no reports on the protonation of halogens, the preparation and isolation of species such as HI_2^+ would appear possible.

1. *Reduction of metal carbonyl dimers*

The ability of the metal carbonyl dimers to be reduced to corresponding monoanions in the presence of appropriate reducing agents represents one of the most striking similarities between these substances and main group pseudohalogens and halogens. Procedures for such reductions have been developed over many years and have been discussed in several reviews [1, 8, 151-153]. Sodium amalgam (1% Na) has been the most commonly used reducing agent and represents a satisfactory procedure if small amounts of covalent mercury compounds can be tolerated [154].

Several alternative procedures are as follows:

$$Co_2(CO)_8 \xrightarrow[THF]{NaK} 2KCo(CO)_4$$ [9]

$$V(CO)_6 + C_2(NH_2)_4 \rightarrow [C_2(NH_2)_4][V(CO)_6]_2$$ [155]

(Only works for most easily reduced carbonyls; gives octamethyloxamidinium^{2+} cations.)

$$[C_5H_5Fe(CO)_2]_2 + 2Mg + 1{,}2\text{-}C_2H_4Br_2 \rightarrow 2BrMgFe(CO)_2C_5H_5 + C_2H_4$$ [156]

A "Grignard" like reagent

$$Mn_2(CO)_{10} + 2Li \xrightarrow{THF} 2LiMn(CO)_5$$ [157]

Recently, the amalgam method has also been used to facilitate reactions of the dimers with a variety of other electropositive metals; e.g., Er [75], Mg [54, 58], Al [52], and Mn [55]. Finely divided lanthanides also interact directly with dimers to form substances that may contain isocarbonyl linkages [56]. (See Section 2.)

The pseudohalogen nature of the metal carbonyl dimers is quite evident from the above reactions with metals. Three additional examples are:

$$Hg + Co_2(CO)_8 \rightarrow Hg[Co(CO)_4]_2$$ [158]

$$Zn + Mn_2(CO)_{10} \xrightarrow[\text{diglyme}]{120^\circ} Zn[Mn(CO)_5]_2$$ [159, 160]

$$Tl + \tfrac{3}{2}Co_2(CO)_8 \xrightarrow[\text{200 atm CO}]{200^\circ} Tl[Co(CO)_4]_3$$ [161]

Other reducing agents such as H_2 (see part 4 below), InBr, GeI_2, $SnCl_2$, $(C_5H_5)_2M$, and $AsCl_3$ have been shown to interact with metal carbonyl dimers as shown by the following equations:

$InBr + Co_2(CO)_8 \rightarrow InBr(Co(CO)_4)_2 \cdot THF$ [162]

$GeI_2 + [C_5H_5Fe(CO)_2]_2 \rightarrow I_2Ge[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$ [163]

$SnCl_2 + [C_5H_5Ni(CO)_2]_2 \rightarrow Cl_2Sn[Ni(CO)C_5H_5]_2$ [164]

$AsCl_3 + [C_5H_5Fe(CO)_2]_2 \xrightarrow{CH_2Cl_2} Cl_2As[C_5H_5Fe(CO)_2]_2{}^+AsCl_4{}^- +$

$Cl_2AsFe(CO)_2C_5H_5$ [165]

$2(C_5H_5)_2M + [C_5H_5Cr(CO)_3]_2 \rightarrow 2(C_5H_5)_2MCr(CO)_3C_5H_5$ [359]
(M = Co, Cr are ionic products; M = V, Ti are reported as containing M—Cr bonds.)

In a related reaction the interhalogenoid $ClFe(CO)_2C_5H_5$ reacts with a transition metal reducing agent, $(C_2H_4)Pt(Ph_3P)_2$ to yield the Pt^{II} derivative $(Ph_3P)_2PtCl[C_5H_5Fe(CO)_2]$ [72]. These interactions have been called oxidative addition or "insertion" reactions and are in a formal sense identical to analogous oxidations by halogens, e.g., $Cl_2 + SnCl_2 \rightarrow SnCl_4$.

Mention should also be made of the compound $SO_2[Fe(CO)_2C_5H_5]_2$ which is similar to main group species SO_2Cl_2 or $SO_2(N_3)_2$ [167]. Though this compound apparently cannot be made by the direct interaction of SO_2 with $[C_5H_5Fe(CO)_2]_2$, it has been prepared by the reaction of SO_2 and $C_5H_5Fe(CO)_2{}^-$, an unusual reaction [168]! Metal hydrides also interact with carbonyl dimers and carbonyl halides to give products analogous to those obtained with halogens. Examples are given by the following equations:

$Co_2(CO)_8 + 2Cl_3SiH \rightarrow 2Cl_3SiCo(CO)_4 + H_2$ [420]

$Mn_2(CO)_{10} + 2Ph_3SiH \rightarrow 2Ph_3SiMn(CO)_5 + H_2$ [421]

$[C_5H_5Cr(CO)_3]_2 + 2Ph_3SnH \rightarrow 2Ph_3SnCr(CO)_3C_5H_5 + H_2$ [359]

$ClMn(CO)_5 + Cl_3GeH \rightarrow Cl_3GeMn(CO)_5 + HCl$ [422]

This general method has been particularly valuable for the preparation of compounds containing silicon to transition metal bonds. In all of these reactions the hydrogen undoubtedly arises from the decomposition of the thermally unstable metal carbonyl hydrides which form as intermediates.

2. *Oxidation of metal carbonyl dimers by halogens or halogenoids*

In section C it was noted that a number of carbonyl dimers, X_2, react with halogens, main group pseudohalogens and other metal carbonyl dimers, Y_2, as follows: $X_2 + Y_2 \rightleftharpoons 2XY$. In addition to those mentioned previously, the mixed carbonyls or "transition metal interhalogenoids" $C_5H_5Fe(CO)_2Mn(CO)_5$, $(OC)_5ReMn(CO)_5$ and $C_5H_5Mo(CO)_3Mn(CO)_5$ [169], and halocarbonyls [170], including $XFe(CO)_2C_5H_5$ [171] and $XMn(CO)_5$ [172] (X = Cl, Br, I) have been prepared by this general route. The close similarity of the reactivity patterns of metal carbonyl dimers and halogens is emphasized by the fact that halohalogenoids including SCNI [173], $BrSCSN_3$ and $ClSCSN_3$ [174] as well as all simple binary interhalogens, IF, BrF, ClF, ICl, IBr and BrCl [175] may also be prepared by direct combination of the parent dimers.

In a related reaction hexamethyldistannane has been shown to react with a variety of metal carbonyl dimers as follows:

$(Me_3Sn)_2 + X_2 \rightarrow 2XSnMe_3$ [176]

($X = Co(CO)_4, Mn(CO)_5, Re(CO)_5, C_5H_5M(CO)_3$ ($M = Mo, W$), C_5H_5NiCO)

Halogens cleave the Sn—Sn bond in hexamethyldistannane to give entirely analogous products [177].

3. Disproportionation of metal carbonyl dimers by Lewis bases.

The close similarity in the chemistry of metal carbonyl dimers and halogens is dramatically evident in the following series of reactions:

$Co_2(CO)_8 + C_5H_{10}NH \rightarrow [Co(CO)_4(C_5H_{10}NH)][Co(CO)_4]$ [178]
(piperidine)

$Mn_2(CO)_{10} + C_4H_9NH_2 \rightarrow [Mn(CO)_5C_4H_9NH_2][Mn(CO)_5]$ [179]
(butylamine)

$X_2 + Me_3N \rightarrow [Me_3NX][X]$ ($X = Cl, Br, I$) [180]

It is likely that other aliphatic amines also interact with $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ to initially give similar species [181]; however, for these monodentate amines, L, only salts of the type $[MnL_6][Mn(CO)_5]_2$ [179] (except for L = NH_3, see 3.c) or $[CoL_6][Co(CO)_4]_2$ [182] have been reported.

The reactions of halogens (Cl_2, Br_2 and I_2) with other alkylamines and ammonia may also involve the formation of analogous ionic intermediates; e.g., $H_3NCl^+Cl^-$, but there appears to be no confirmation of this point in the literature.

The relative susceptibility of unsubstituted metal carbonyl dimers and paramagnetic monomers to Lewis base induced disproportionation is observed to be: $V(CO)_6 > Co_2(CO)_8 > Mn_2(CO)_{10} >> Re_2(CO)_{10}$. Since the relative tendency for the halogens to undergo disproportionation increases with increasing ease of reduction ($Cl_2 > Br_2 > I_2$) [183], it might be anticipated that a similar relationship holds among the carbonyl dimers. This appears to be the case since the relative ease in reducing metal carbonyl dimers electrochemically has been shown to be $Co_2(CO)_8 > [C_5H_5Cr(CO)_3]_2 > [C_5H_5Mo(CO)_3]_2 > [Mn(CO)_5]_2 > [C_5H_5Fe(CO)_2]_2 > [Re(CO)_5]_2 > [C_5H_5Ni(CO)]_2 > [C_5H_5Ru(CO)_2]_2$ [184]. An independent polarographic study has also shown that $V(CO)_6$ in methylene chloride is reversibly reduced more easily than $Co_2(CO)_8$ [78]. Because of the few studies reported on attempts to disproportionate substituted dimers (see D.3.d) it is not possible to assess their relative tendency to undergo disproportionation. However, the above data suggest that $[C_5H_5Cr(CO)_3]_2$ should be quite base sensitive. Perhaps this accounts for some of the difficulties experienced in preparing this dimer in high yields [140].

Whenever a Lewis base attacks a metal carbonyl, either substitution and/or disproportionation can occur. With hard bases such as those containing oxygen or nitrogen donor functions, disproportionation of neutral carbonyl dimers is favored over substitution, except with $Re_2(CO)_{10}$. For example, in the presence of hydroxide ion all unsubstituted carbonyl dimers undergo disproportionation reactions; however, $Re_2(CO)_{10}$ behaves differently from $V(CO)_6$,

$Mn_2(CO)_{10}$ and $Co_2(CO)_8$ in that reduction of the rhenium is accompanied by oxidation of a CO group according to the equation:

$$Re_2(CO)_{10} + 4OH^- \rightarrow [Re_2(CO)_9]^{2-} + CO_3^{2-} + 2H_2O$$

The dianion is then rapidly oxidized by water to the unusual Re^{II} anion, $Re_2(CO)_8O_2H^-$ [185]. Softer bases such as phosphines, isocyanides and phosphites often give substitution products with $V(CO)_6$ and $Co_2(CO)_8$ and almost exclusively give them with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The disproportionation reactions of $V(CO)_6$, $Co_2(CO)_8$, $Mn_2(CO)_{10}$ and some cyclopentadienyl substituted dimers will now be discussed in some detail. Other than the attack of hydroxide ion on $Re_2(CO)_{10}$ mentioned previously, there appear to be no reports of Lewis base induced disproportionations of this substance. Disproportionation reactions of metal carbonyls have been discussed previously in other review articles [8, 151, 152].

Since no complete review of the chemistry of $V(CO)_6$ exists in the literature, the following description will be more comprehensive than those given for the other carbonyls in this section.

a. Vanadium hexacarbonyl. Paramagnetic $V(CO)_6$ is the most reactive unsubstituted neutral carbonyl known and reacts with practically all solvents in which it is soluble except saturated hydrocarbons. A compilation of its disproportionation reactions is given in Fig. 1. Even in weakly Lewis basic solvents such as benzene or toluene it slowly disproportionates, giving moderate yields of the salt $[\text{arene-}V(CO)_4][V(CO)_6]$ [189, 190]. Cycloheptatriene also causes partial disproportionation to give $[C_7H_7VC_7H_8][V(CO)_6]$ as well as the substitution product $C_7H_7V(CO)_3$ [191]. There appear to be no reports in the scientific literature on the reactions of other neutral olefins with $V(CO)_6$; however, in view of the above results some disproportionation of $V(CO)_6$ in their presence would be anticipated. In the presence of hard bases such as diethyl ether, THF, ammonia, alcohols, etc., practically instantaneous disproportionation occurs at room temperature to give salts of the type $[VL_n][V(CO)_6]_2$,

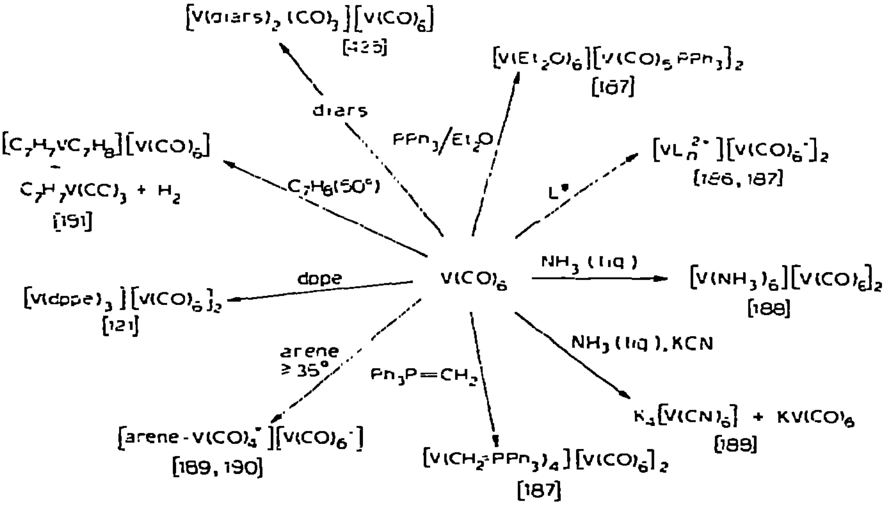


Fig. 1. Disproportionation reactions of vanadium hexacarbonyl (references in brackets).

where *n* varies from 2 to 6 (see Fig. 1.). By analogy with the manganese and cobalt systems it seems quite possible that initially a salt such as $V(CO)_6L^+V(CO)_6^-$ forms. Each vanadium thereby attains an 18 electron configuration. Additional base may then attack the cation causing further disproportionation to a vanadium(II) species.

Some of the disproportionation reactions of vanadium hexacarbonyl are particularly novel. For example, substituted carbonyl anions can result from the reaction of $V(CO)_6$ with phosphines under appropriate conditions. Whereas an excess of triphenylphosphine and $V(CO)_6$ in hexane forms *trans*-$V(CO)_4(Ph_3P)_2$ [192], an equimolar mixture of the reactants in ether gives $[V(Et_2O)_6][V(CO)_5PPh_3]_2$ [187]. The latter must form from the disproportionation of a neutral substituted vanadium carbonyl, either $V(CO)_4(Ph_3P)_2$ or the unknown $V(CO)_5Ph_3P$, since $V(CO)_6^-$ undergoes phosphine substitution only under photolytic conditions [193]. In this regard it is interesting to note that $V(CO)_4(Ph_3P)_2$ is reduced by sodium amalgam in benzene [187] or ethanol [192] to yield $V(CO)_5PPh_3^-$ instead of the expected $V(CO)_4(Ph_3P)_2^-$. Attempts to prepare the latter species by prolonged photolyses of THF solutions of $V(CO)_5Ph_3P^-$ in the presence of large excesses of triphenylphosphine have also failed [78], although it is known that dppe readily gives $V(CO)_4dppe^-$ [193]. The latter anion was first prepared by the disproportionation of paramagnetic $V(CO)_4dppe$ with α,α'-bipyridyl in benzene according to the equation:

$$3V(CO)_4dppe + 3bipy \xrightarrow{75^\circ} [V(bipy)_3][V(CO)_4dppe]_2 + dppe + 4CO \qquad [121]$$

Neutral $V(CO)_4dppe$ is far more stable towards donor solvents than $V(CO)_6$; for example, it is stable for hours in dry, peroxide-free THF [78]. Unusual V^{II} cations, such as tetrakis(methylenetriphenylphosphorane)vanadium(II), can also form in the disproportionation of $V(CO)_6$ with appropriate bases [187]. The structure of this cation, apparently unknown, could involve either V—C or V—P bonds.

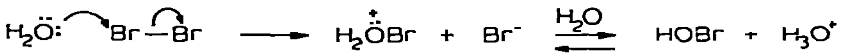
b. Dicobalt octacarbonyl. This substance, like $V(CO)_6$, is extremely sensitive to Lewis bases. For example, while $Mn_2(CO)_{10}$ remains unchanged for days in dry, peroxide-free tetrahydrofuran, $Co_2(CO)_8$ under identical conditions at room temperature forms detectable amounts of $Co(CO)_4^-$ within minutes [78]. Although $Co_2(CO)_8$ has not been reported to undergo disproportionation reactions in the presence of olefins or arenes [152, 194a] (this type of interaction appears to be unique with $V(CO)_6$), high pressures of the extremely weak base CO are considered to form $[Co(CO)_5][Co(CO)_4]$, a very unstable ionic species [194]. Benzene or toluene at 80° in the presence of $AlBr_3$, however, reacts with $Co_2(CO)_8$ [195] or $Hg(Co(CO)_4)_2$ [196] to give $[Co_3(CO)_2arene_3]X$, where X = Br or $Co(CO)_4$, respectively. The diamagnetic cation contains two triply bridging CO groups symmetrically disposed above and below a triangular array of cobalt atoms, a structure similar to that of paramagnetic $Ni_3(CO)_2(C_5H_5)_3$ [197]. Salts also form when $Co_2(CO)_8$ reacts with phosphines, arsines, and stibines at low temperature; e.g., $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ [198]. Although monophosphine cations apparently have not been isolated in these disproportionation reactions, they are likely intermediates. The monotriphenylphosphine cation has been prepared by an indirect route:

$$Ph_3PCo(CO)_3CO(OEt) + 2HCl \xrightarrow{-50^\circ} [Ph_3PCo(CO)_4][HCl_2] + EtOH \qquad [199]$$

At higher temperatures $[Co(CO)_3(Ph_3P)_2]^+$ is attacked by the nucleophilic $[Co(CO)_4]^-$ to yield the substitution product $[Co(CO)_3PPh_3]_2$, which, unlike solid $Co_2(CO)_8$, contains no bridging carbonyls. Isocyanides also attack $Co_2(CO)_8$ to give a $Co^{I}Co^{-I}$salt, but in this case carbonyl displacement in the cation is complete:

$$Co_2(CO)_8 + 5RNC \rightarrow [Co(CNR)_5][Co(CO)_4] + 4CO \qquad [200]$$

The disproportionation of halogens in neutral or basic aqueous solutions to give hypohalous acid (or hypohalites) and halide ion is often cited as another important criterion for a substance to be considered a pseudohalogen [11]. If the initial attack of water (or hydroxide ion) on bromine is analogous to that of trimethylamine on bromine it can be represented by the equation:



$$H_2\ddot{O}{:}\ Br{-}Br \longrightarrow H_2\overset{+}{\ddot{O}}Br + Br^- \xrightleftharpoons{H_2O} HOBr + H_3O^+$$

Such an initial step seems reasonable in that the existence of H_2OBr^+, a bromooxonium ion, has been confirmed in acidified aqueous solutions of HOBr [201]. Water does attack $Co_2(CO)_8$, albeit slowly, because the carbonyl is practically insoluble in this medium, but only salts of the type $[Co(H_2O)_n][Co(CO)_4]_2$ have been isolated [202]. However, the presumed initial intermediate in this reaction is $Co(CO)_4OH_2^+$ or $Co(CO)_4OH$ [204]. The latter species can be compared with HOI, also an extremely unstable substance which readily disproportionates to iodide and iodate [203]. The detection of thermally unstable salts of the type $[Co(CO)_4ROH][Co(CO)_4]$ and $[Co(CO)_4(C_5H_{11}N)][Co(CO)_4]$ ($C_5H_{11}N$ = piperidine) generated from the interaction of alcohols [204] and piperidine [178], respectively, provides additional support for the suggestion that water as well as other hard Lewis bases interact with $Co_2(CO)_8$ to initially form salts of the type $[Co(CO)_4B][Co(CO)_4]$ [178]. These reactions also nicely demonstrate that $Co_2(CO)_8$ behaves in a manner expected of a transition metal pseudohalogen.

c. Diamanganese decacarbonyl. A large variety of hard bases including pyridine, morpholine, piperidine and ethylenediamine cause disproportionation of $Mn_2(CO)_{10}$ and give salts of the type $[MnL_n][Mn(CO)_5]_2$, which probably form via initial intermediates of the type $[Mn(CO)_5L][Mn(CO)_5]$. As indicated in the introduction such an intermediate has been isolated for L = butylamine [179]. A more highly substituted salt $[Mn(CO)_3(NH_3)_3][Mn(CO)_5]$, obtained from the action of liquid ammonia on the dimer, has also been reported [205]. These reactions require much more vigorous conditions than analogous ones conducted with $Co_2(CO)_8$ [206]. Isocyanides also give disproportionation reactions with $Mn_2(CO)_{10}$, but phosphines and softer Lewis bases normally only form nonionic substituted products [206, 207]. Disproportionation of $Mn_2(CO)_{10}$ in the presence of dppe (1,2-diphenylphosphinoethane) reportedly occurs, however, to give $[Mn(CO)_2(dppe)_2][Mn(CO)_5]$ [208].

d. Substituted dimers. Few reports on disproportionation reactions of substituted dimers such $[C_5H_5M(CO)_3]_2$ (M = Cr, Mo, W) and $[C_5H_5Fe(CO)_2]_2$ have appeared in the literature. The latter has been reported to slowly react with dmpe (1,2-bis(dimethylphosphino)ethane) in benzene at room temperature to yield the usual salt $[C_5H_5Fe(CO)dmpe][C_5H_5Fe(CO)_2]$ [209]. Only recently have other salts containing $C_5H_5Fe(CO)_2^-$ been characterized [9].

These were prepared by direct reduction of the dimer. The Group VIb substituted dimers are more susceptible to disproportionation than the iron dimer. For example, $[C_5H_5Mo(CO)_3]_2$ reacts with Ph_3P, Et_3P, Bu_3P, dppe [210] and dmpe [209] under photolytic conditions to give ionic species of the type $[C_5H_5Mo(CO)_2L_2][C_5H_5Mo(CO)_3]$. No similar studies of the presumably more base sensitive chromium dimer have appeared in the literature. Also, there appear to be no reports on the interaction of amines or other hard bases with these species [211].

e. Halometal carbonyls and related species. Disproportionation reactions of halometal carbonyls are well known and closely related to those of the dimers. The halogen, being the more electronegative group in these compounds, is invariably reduced. Examples of such interactions are the following:

$C_5H_5Fe(CO)_2Cl + H_2O \rightarrow C_5H_5Fe(CO)_2OH_2^+\,Cl^-$ [212, 423]

$C_5H_5Mo(CO)_3Cl + 2PPh_3 \rightarrow C_5H_5Mo(CO)_2(PPh_3)_2^+\,Cl^-$ [213]

$Mn(CO)_5Cl + en \rightarrow Mn(CO)_3en^+Cl^-$ [214]

$Re(CO)_5I + dppe \rightarrow Re(CO)_2(dppe)_2^+I^-$ [215]

$Mn(CO)_5I + C_6H_6 \rightarrow C_6H_6Mn(CO)_3^+\,I^-$ [216]

Very weak bases can also cause similar disproportionations in the presence of a halide acceptor such as $AlCl_3$, $FeCl_3$, etc. For example:

$C_5H_5Fe(CO)_2Cl + C_2H_4 + AlCl_3 \rightarrow [C_5H_5Fe(CO)_2C_2H_4][AlCl_4]$ [217]

$Re(CO)_5Cl + CO + AlCl_3 \rightarrow [Re(CO)_6][AlCl_4]$ [218]

$Mn(CO)_5Cl + C_4H_4S + AlCl_3 \rightarrow [Mn(CO)_3C_4H_4S][AlCl_4]$ [219]
(C_4H_4S = thiophene)

$C_5H_5Mo(CO)_3Cl + C_6H_6 + AlCl_3 \rightarrow [C_5H_5Mo(CO)C_6H_6][AlCl_4]$ [220]

Many other related reactions are discussed in a recent review on metal carbonyl cations [221].

Transition metal "interhalogenoids" or mixed metal carbonyls such as $(OC)_5MnRe(CO)_5$ or $C_5H_5Fe(CO)_2Mn(CO)_5$ would also be expected to disproportionate in the presence of appropriate Lewis bases. Although such reactions apparently have not been studied, it is expected that the more easily reduced carbonyl grouping will form the anion. For example, since $Co_2(CO)_8$ is more easily reduced than $[C_5H_5Fe(CO)_2]_2$ [184], it is expected that $C_5H_5Fe(CO)_2$-$Co(CO)_4$ [222] in the presence of a hard base, B, should give salts of the type $[C_5H_5Fe(CO)_2B][Co(CO)_4]$, provided substitution does not occur exclusively.

4. *Hydrogenation of dimers.*

A number of metal carbonyl dimers as well as the 17 electron radical anion $Co(CN)_5^{3-}$ have been shown to react directly with hydrogen to form metal hydrides. Some of these were discussed in section B.

$2Co(CN)_5^{3-} + H_2 \xrightarrow[\text{atm. pressure}]{\text{room temp.}} 2HCo(CN)_5^{3-}$ [223]

$Co_2(CO)_8 + H_2 \xrightarrow{110^\circ, CO, H_2} 2HCo(CO)_4$ [90]

$[C_5H_5Cr(CO)_3]_2 + H_2 \xrightarrow[70^\circ]{150\ \mathrm{atm}} 2HCr(CO)_3C_5H_5$ [224]

$Mn_2(CO)_{10} + H_2 \xrightarrow[250\ \mathrm{atm}, 200^\circ]{CO} 2HMn(CO)_5$ [225]

In the absence of excess CO pressure, condensation reactions often occur. For example, $Re_2(CO)_{10}$ can be hydrogenated at one atmosphere pressure in hydrocarbon solvents at 150-170° to give either $H_3Re_3(CO)_{12}$ or $H_4Re_4(CO)_{12}$ instead of the uncondensed $HRe(CO)_5$ [89].

5. Reactions of dimers with olefins and acetylenes

Since chlorine, bromine and thiocyanogen readily add to olefins to give vicinal-disubstituted products, it might be anticipated that under certain conditions metal carbonyl dimers, as well as halometal carbonyls, would also react to give analogous 1,2-addition or insertion species. Although metal carbonyl hydrides readily form olefin insertion products of this type, $Co_2(CO)_8$ is apparently the only carbonyl dimer reported to give a similar product with an olefin:

$Co_2(CO)_8 + F_2C{=}CF_2 \rightarrow (OC)_4CoCF_2CF_2Co(CO)_4$ [226, 227]

Attempts to prepare 1,2-bis(carbonylmetal)ethane derivatives by direct reaction of dimers with olefins or by reaction of 1,2-dihaloethane with carbonylmetallate monoanions have resulted either in formation of products arising from initial substitution of CO groups by olefin or ethylene and dimer, respectively. For example:

$Mn_2(CO)_{10} + C_4H_6 \xrightarrow{h\nu} (C_4H_6)(OC)_3MnMn(CO)_5$ [228]
(butadiene)

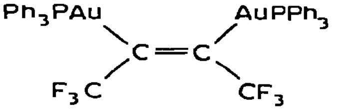
$2C_5H_5Fe(CO)_2^- + BrCH_2CH_2Br \rightarrow C_2H_4 + [C_5H_5Fe(CO)_2]_2$ [229]

In a related observation, $Me_3SnMn(CO)_5$ was found to react with C_2F_4 to give the insertion product $Me_3SnCF_2CF_2Mn(CO)_5$, whereas treatment with C_2H_4 under photolytic conditions gave only the substitution product $Me_3SnMn(CO)_4(\pi\text{-}C_2H_4)$ [230]. At least one binuclear organo transition metal ethane derivative has been reported: the unstable $[(C_5H_5)_2ZrCl]_2C_2H_4$, prepared from $(C_5H_5)_2ZrCl_2$ and triethylaluminum [231].

Another possible route to 1,2-bis(carbonylmetal)ethane species involves the attack of metal carbonyl anions on metal carbonyl olefin cations, such as $[C_5H_5(CO)_2Fe(\pi\text{-}C_2H_4)]^+$. Although at low temperature the reaction could give a binuclear σ complex, at normal temperatures the ethylene or olefin would undoubtedly be eliminated. It is interesting to note that carbonyl olefin cations are electronically equivalent to similar halonium ions e.g. $[Br(\pi\text{-}C_2H_4)]^+$, which are intermediates in the halogenation of olefins in the absence of free radicals. The olefin may be considered to cause an initial disproportionation or heterolytic cleavage of the halogen, which results in the formation of the halonium ion. Such ionic intermediates may also occur in some addition or insertion reaction with metal carbonyl derivatives.

Acetylenes have been reported to undergo only substitution reactions with carbonyl dimers, particularly $Co_2(CO)_8$ [152]. Since the 17 electron species $Co(CN)_5^{3-}$ reacts with acetylene to give the 1,2-disubstituted ethylene,

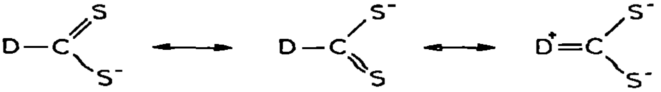
$H_2C_2(Co(CN)_5)_2^{6-}$ [232], it seems possible that metal carbonyl radicals (e.g., $Mn(CO)_5\cdot$ [136a]) could also react in the same fashion. The cobalt cyanide anion also reacts with C_2F_4 to give a product analogous to that described earlier for $Co_2(CO)_8$ [233]. At least one other 1,2-disubstituted organometal ethylene has also been reported:



[234]

E. Adducts with unsaturated species

Since certain pseudohalides, notably N_3^- and CN^-, form 1/1 adducts with carbon disulfide [236] it might be expected that metal carbonyl monoanions should form analogous products. In fact, only the most reactive anions including $C_5H_5Fe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_4P(C_6H_{11})_3^-$ and $C_5Me_5Fe(CO)_2^-$ form anionic species of the type MCS_2^-, where M is the metal carbonyl moiety. Like some of their main group analogues, including thioxanthates, dithiocarbamates, etc., they function as uninegative mono- or bi-dentate ligands in the presence of appropriate acceptor groups. For example, complexes of the type $Ph_3SnS(S)CM$ and $Cr(S_2CM)_3$ have been prepared and characterized. In the former case the ligand is monodentate; in the latter case it is bidentate [235]. These new transition metal containing ligands may be considered to be organometallic analogues of dithiocarbamates or dithioacid anions [236]. For example, the following resonance forms may all be important in describing the electronic configuration of the anion:



where D is some donor atom such as nitrogen or a transition metal in a low formal oxidation state. For a transition metal the last resonance form represents metal "back donation." Similar forms have been previously invoked to explain myriad features of carbonyl complexes such as the abnormally low ketonic CO stretching frequencies in acylmetal carbonyls and the M—C multiple bond orders in transition metal carbenes and carbonyls.

Another similar reaction has been reported recently between SO_2 and $C_5H_5Fe(CO)_2^-$ to give $C_5H_5Fe(CO)_2SO_2^-$ [237]. Methylation of this anion gives $C_5H_5Fe(CO)_2SO_2CH_3$, suggesting that the anionic adduct has an Fe—S bond. Although the generality of this reaction remains unknown, it seems likely that a variety of other unsaturated molecules containing electronegative atoms will interact with at least the most reactive metal carbonyl monoanions.

III. Carbonyl dianions

Much less is known about the chemistry of the metal carbonyl dianions than that of the monoanions; however, the available information is largely consistent with a description of these species as transition metal pseudochalcogenides. For example, there exist a number of sulfur compounds in which the sul-

TABLE 3

SULFUR COMPOUNDS AND $Fe(CO)_4$ ANALOGUES[a]

S, atomic sulfur	[239]	$Fe(CO)_4$[b]	[240]
S^{2-}		$Fe(CO)_4^{2-}$	[241]
HS^-		$HFe(CO)_4^-$	[242]
H_2S		$H_2Fe(CO)_4$	[243]
S_2^{2-}		$[Fe(CO)_4]_2^{2-}$	[244]
HS_2^-		$HFe_2(CO)_8^-$	[238]
Cl_2S		$Cl_2Fe(CO)_4$	[245]
Cl_2S_2[c]		$I_2[Fe(CO)_4]_2$[c]	[246]
BrS^-[d]	[255]	$IFe(CO)_4^-$[d]	[247]
NCS^-		$NCFe(CO)_4^-$	[248]
HgS		$HgFe(CO)_4$	[249]
OCS		$OCFe(CO)_4$	[8]
Ph_3PS		$Ph_3PFe(CO)_4$	[250]
CH_3NCS		$CH_3NCFe(CO)_4$	[66]
CH_3COS^-, thioacetate		$CH_3COFe(CO)_4^-$	[251]
$(CH_3O)C_6H_5CS$, methylthiobenzoate		$(CH_3O)C_6H_5CFe(CO)_4$	[252]
C_2H_4S, ethylene sulfide		$(\pi\text{-}C_2H_4)Fe(CO)_4$	[253]
$(Ph_3Sn)_2S$	[256]	$(Ph_3Sn)_2Fe(CO)_4$	[254]

[a] Only the less common sulfur derivatives are referenced. [b] An intermediate generated by thermal or photolytic decomposition of $Fe(CO)_5$. [c] I_2S_2 is unknown; only $I_2[Fe(CO)_4]_2$ has been reported. [d] IS^- and $BrFe(CO)_4^-$ are unknown.

fur atom may be formally replaced by a $Fe(CO)_4$ group without drastically altering the structure or the reactivity patterns of the species. A number of examples of sulfur compounds and their $Fe(CO)_4$ analogues are shown in Table 3.

The ability of the $Fe(CO)_4$ group to mimic the behavior of a sulfur atom arises because they are electronically equivalent species in the sense that both $Fe(CO)_4$ and S are two electrons short of attaining a closed-shell configuration. On this basis these species may be anticipated to display carbenoid behavior. Although the relationship between the reactivity patterns of these $Fe(CO)_4$ derivatives and their electronically equivalent main group counterparts has not been explored extensively or systematically, there are a number of reactions of sulfur compounds and their $Fe(CO)_4$ analogues which suggest that the relationship is a meaningful one. These will be described later.

There are several known monomeric carbonyl dianions, including $Fe(CO)_4^{2-}$ [8], $Ru(CO)_4^{2-}$ [257], $Os(CO)_4^{2-}$ [394], $Cr(CO)_5^{2-}$ [259], $Mo(CO)_5^{2-}$ [260], $W(CO)_5^{2-}$ [261], and $C_5H_5V(CO)_3^{2-}$ [262]. The latter is apparently the only known cyclopentadienyl-substituted monomeric dianion. Other known substituted dianions include $Ni(CO)_3(PhP)_3^{2-}$, $Fe(CO)_3(PhP)_3^{2-}$ [426], $(\pi\text{-}B_9C_2H_{11})M(CO)_3^{2-}$ (M = Mo, W) [427], and cyanide-substituted species, e.g., $V(CO)_5CN^{2-}$ [263] and $Co(CO)_2(CN)_3^{2-}$ [264]. The chemistry of the latter two species is undoubtedly different from that of binary or cyclopentadienyl-substituted carbonyl monomeric dianions. The nitrogen of the cyanide group is probably the strongest donor site in these species as it is in coordinatively saturated cyanide-substituted carbonyl monoanions [64].

The chemistry of $Fe(CO)_4^{2-}$ has been heavily investigated, at least with respect to that of the other monomeric dianions. The available information on the chemistry of these other species, however, is also largely consistent with a description of these species as transition metal pseudochalconides.

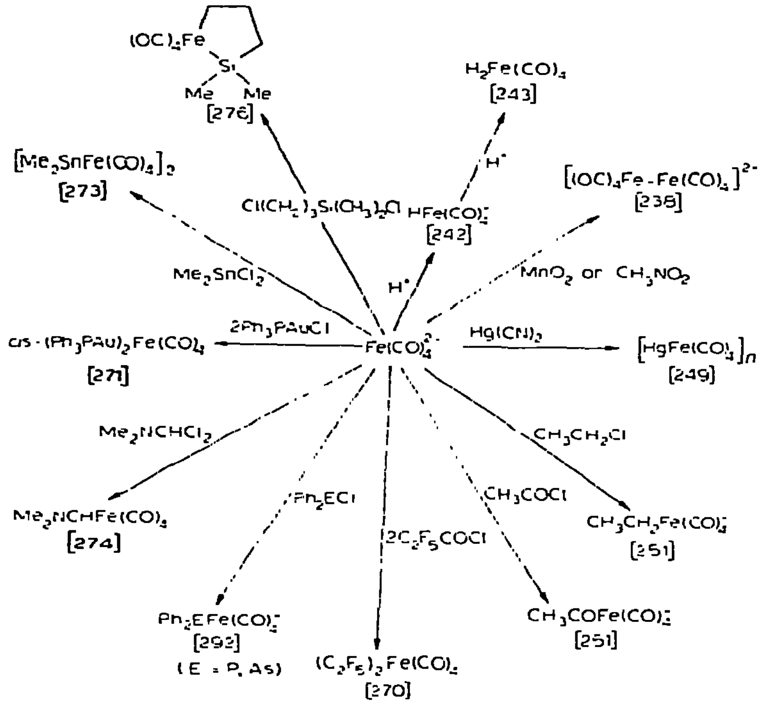


Fig. 2. Representative chemistry of $Fe(CO)_4^{2-}$ (references in brackets).

The chemistry of these anions as well as a number of their derivatives will now be discussed to emphasize their similarity to electronically equivalent main group species. Since the chemistry of $Fe(CO)_4^{2-}$ has received the most attention, it will be discussed first. Except for recent work on the use of this ion in organic syntheses [315] and very early work described previously in another review [8], this treatment is intended to be comprehensive.

A. Tetracarbonyl metallates of Fe, Ru and Os

1. Preparation and chemistry of $Fe(CO)_4^{2-}$

A number of methods for the preparation of this substance have been described [8]. Also, a new large-scale preparation of $Na_2Fe(CO)_4$ from the reduction of $Fe(CO)_5$ with sodium dispersion in THF, using benzophenone ketyl as a homogeneous reduction catalyst, has been noted recently [241].

Some representative reactions of this dianion are given in Fig. 2. The sulfide anion also has been shown to give analogous sulfur derivatives with many of the electrophilic agents shown in Fig. 2. For example, the sulfide ion may be protonated to give HS^- and H_2S. The dissociation constants for H_2S ($K_1 = 5.7 \times 10^{-8}$, $K_2 = 1.2 \times 10^{-15}$) [265], are close to those reported for $H_2Fe(CO)_4$($K_1 = 3.6 \times 10^{-5}$ and $K_2 = 1 \times 10^{-14}$) [266]. Both acids are also volatile, malodorous substances. Although such similarities may be surprising, they emphasize the ability of the $Fe(CO)_4$ group to mimic the behavior of a sulfur atom in derivatives.

Sulfide ion and $Fe(CO)_4^{2-}$ can also be oxidized by appropriate agents to

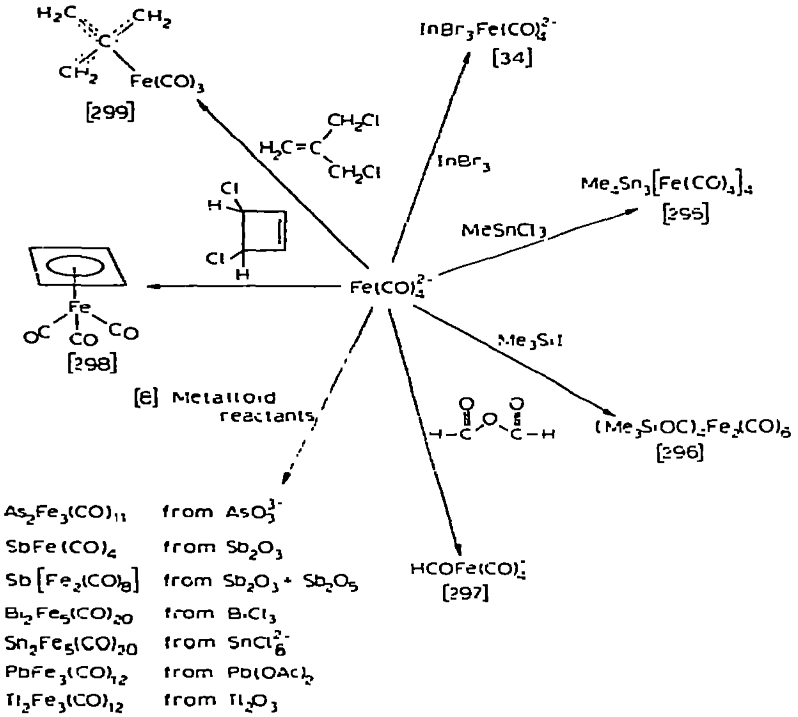


Fig. 3. Novel reactions of $Fe(CO)_4^{2-}$ (references in brackets).

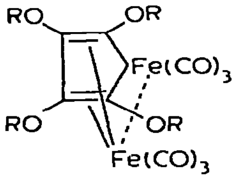
give dimeric dianions. Another important similarity is the reaction of S^{2-} and $Fe(CO)_4^{2-}$ with a variety of mercury(II) salts to yield the insoluble, polymeric species, HgS and $HgFe(CO)_4$ [249]. The dark yellow iron compound is thought to have a structure containing zigzag chains, not unlike those found in red HgS (cinnabar). A black Pb^{II} derivative, $[PbFe(CO)_4]_n$ is also known [267] and is formally analogous to PbS. The interaction of $Fe(CO)_4^{2-}$ with other main group metal species gives a bewildering variety of substances whose structures are generally unknown (see Fig. 3.). Their stoichiometries are often unrelated to those of corresponding sulfides, which suggests that many of these contain metal cluster units. These have been discussed in detail previously [76].

The interactions of alkyl and acyl halides with $Fe(CO)_4^{2-}$ have been investigated recently. Although iron species corresponding to monothiocarboxylate and alkylmercaptide ions have been isolated and characterized [251], neutral derivatives such as $R_2Fe(CO)_4$ or $(RCO)_2Fe(CO)_4$, which correspond to dialkyl sulfides or diacyl sulfides, are unknown and, if formed, apparently undergo rapid reductive eliminations as follows:

$$RCOFe(CO)_4^- + R'Cl \rightarrow [RCOFe(CO)_4R'] \rightarrow RCOR' + [Fe(CO)_4] + Cl^- \quad [269]$$

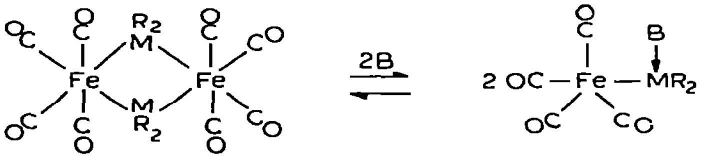
However, perfluoroalkyl derivatives such as $(C_2F_5)_2Fe(CO)_4$ and $(C_3F_7)_2Fe(CO)_4$, prepared by treating the corresponding perfluoroacyl chloride with the dianion, are reported as air-stable, crystalline substances at room temperature [270]. The preparations of mixed species such as *cis*-$(Ph_3PAu)_2Fe(CO)_4$ [271], *cis*-

$(CH_3Hg)_2Fe(CO)_4$ [272], $(o\text{-triars})_2Fe(CO)_4$ [300], and $(Ph_3M)_2Fe(CO)_4$ (M = Sn, Pb) [301] by treatment of the corresponding metal halides or hydroxides with $Fe(CO)_4^{2-}$ or $HFe(CO)_4^-$, respectively, have also been reported. Analogous sulfur compounds, $(M)_2S$, where M = Ph_3Sn, Ph_3PAu, etc., have been prepared by similar procedures. An important alternative route to $M_2Fe(CO)_4$ species, where M is a substituted main group element, is the reaction of $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with the corresponding halide. Solvent-sensitive silyl derivatives such as $(R_3Si)_2Fe(CO)_4$, where R is an organic group or halogen, have been prepared by this route [302]. It is interesting to note that attempts to obtain $(Me_3Si)_2Fe(CO)_4$ by the interaction of $Fe(CO)_4^{2-}$ with Me_3SiI in tetrahydrofuran yielded an entirely different product, recently found by X-ray crystallography to contain a substituted ferracyclopentadiene ring [296] as shown below.



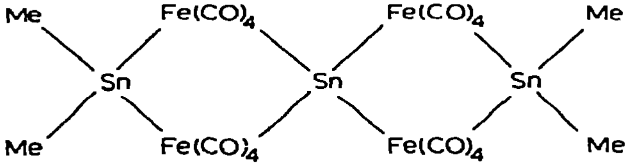
(R = $SiMe_3$)

The reactions of R_2MCl_2, (R = CH_3, C_6H_5; M = Ge, Sn) with $Fe(CO)_4^{2-}$ have been studied extensively and yield dimeric species containing bridging dialkylmetal or diarylmetal groups [273]. These are cleaved by base as follows:



(M = Sn, Ge, R = CH_3,C_6H_5; B = THF, pyridine, etc)

Species of the same general stoichiometry such as $B_2CdFe(CO)_4$, where B = pyridine, ammonia, γ-picoline, ½(ethylenediamine), ½(bipyridyl) or ½ (phenanthroline) may be prepared by interaction of an appropriately complexed metal cation with $HFe(CO)_4^-$ in aqueous solution [303]. The structures of these and similar, presumably di- or poly-meric, species are unknown. Related substances have also been prepared by direct interaction of a metal or alkyl halide with $Fe(CO)_5$. These include $[R_2MFe(CO)_4]_2$, M = Ge, Sn; R = CH_3, C_2H_5 from $R_2Sn(vinyl)_2$ [304], $[Bu_2SnFe(CO)_4]_2$ from Bu_3SnCl [305] and $[R_2SnFe(CO)_4]_2$ from R_2SnH_2 [306]. A red crystalline compound of stoichiometry $Me_4Sn_3[Fe(CO)_4]_4$ was obtained in about 10% yield from the reaction of $Na_2Fe(CO)_4$ and $MeSnCl_3$. This compound has a structure containing four $Fe(CO)_4$ groups bridging three tetrahedrally coordinated tin groups,



Studies on analogous sulfur compounds, $[R_2MS]_n$, $n = 3$, for M = Sn and R = C_6H_5 [281] have not been reported; they may behave similarly. Also sulfur compounds of the type $R_4Sn_3S_4$, although apparently unreported, should be capable of existence. Only one communication on the reaction of $Fe(CO)_4^{2-}$ with an organic geminal dihalide has been reported [274]:

$$Me_2NCHCl_2 + Na_2Fe(CO)_4 \rightarrow Me_2NCHFe(CO)_4 + 2NaCl$$

The formation of other coordinated carbenes by this route could be of general synthetic importance.

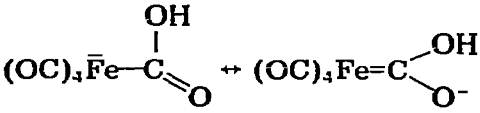
Two reactions with unsaturated organic dihalides have also been reported (Fig. 3). Thus, 3,4-dihalocyclobutenes and 1,1-bis(chloromethyl)ethylene yield π-cyclobutadienetricarbonyliron [298] and π-tris(methylenemethane)tricarbonyliron [299]. In these reactions a carbonyl group is eliminated, thereby increasing the electron requirement of the iron center by two. Although the $Fe(CO)_4^{2-}$ may initially behave as a pseudochalcogen in these reactions, the final products are clearly unprecendented in main group chemistry.

The interaction of neutral Lewis acids with $Fe(CO)_4^{2-}$ has received little attention. Only one example of such an adduct has been reported, $Br_3InFe(CO)_4^{2-}$ [34]. In contrast, several adducts of this type have been formed with carbonylmonoanions (cf. I.A.1.b). Reports on the displacement of groups other than halides by $Fe(CO)_4^{2-}$ are also uncommon. One important recent example, however, is the formation of $HCOFe(CO)_4^-$ by the reaction of the dianion with acetic anhydride [297]. In principle, this formyl anion could also be prepared by the reaction of $Fe(CO)_5$ with an ionic hydride.

2. *The chemistry of some derivatives of* $Fe(CO)_4^{2-}$

Earlier it was indicated that analogous sulfur and tetracarbonyliron derivatives exist since they contain electronically equivalent units. A potentially far more significant observation, however, is that several of these derivatives have strikingly similar reactivity patterns, provided only reactions are considered in which loss of carbon monoxide from the $Fe(CO)_4$ unit or valence shell expansion of the sulfur does not occur. In this context, the $Fe(CO)_4$ group may profitably be considered a large polarizable pseudochalcogen. On this basis $Fe(CO)_5$ and $Fe(CO)_4$ should have reactivity patterns analogous to those of carbonyl sulfide and atomic sulfur, respectively. Figures 4 and 5 show that for a number of reactions such analogies are valid.

a. Comparison of the reactivity patterns of SCO and $Fe(CO)_5$. Perhaps the most striking similarity in the chemistry of SCO and $Fe(CO)_5$ is their reaction with hydroxide ion as shown in Fig. 4. Presumably in both cases the hydroxide ion initially attacks the electrophilic carbonyl group to give an intermediate containing a carboxyl function which then collapses to the observed products. The anionic intermediate may either be protonated at the iron site (as shown) or on an oxygen to give a resonance-stabilized intermediate as follows:



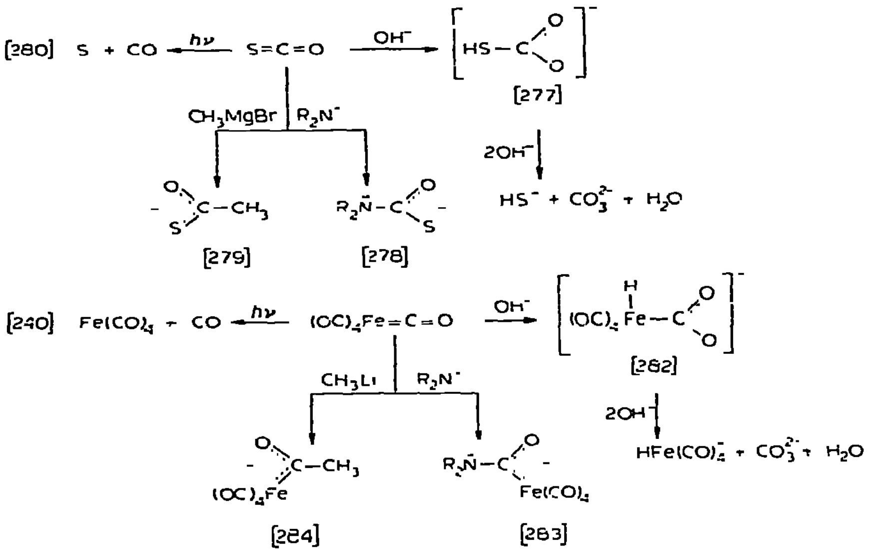


Fig. 4. Comparison of the reactivity patterns of SCO and $Fe(CO)_5$ (references in brackets).

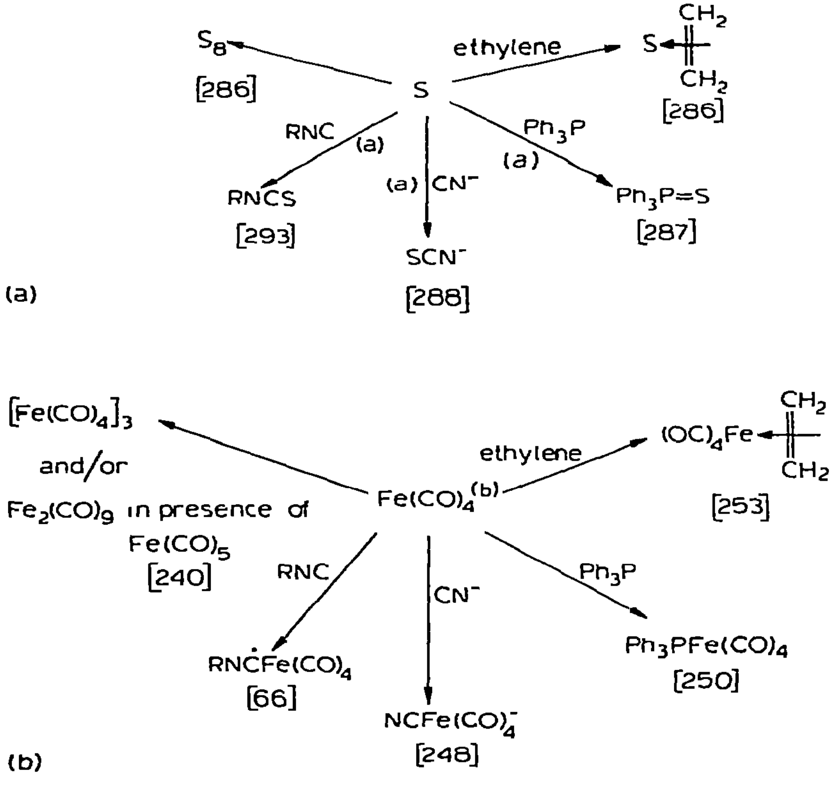


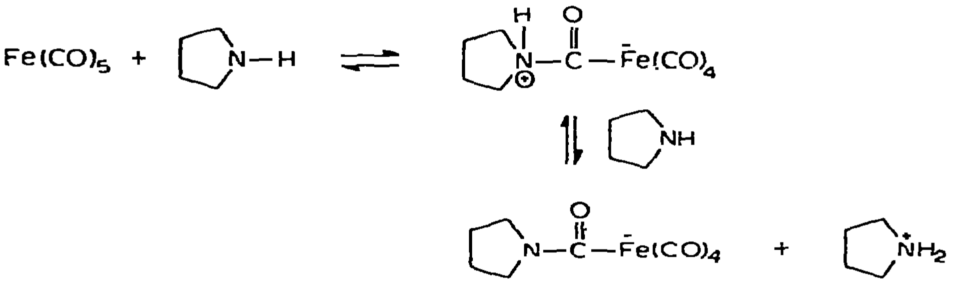
Fig. 5. Comparison of sulfur and $Fe(CO)_4$ chemistry (references in brackets). (a) Reactions of base with S_8: atomic sulfur would undoubtedly yield the same product. (b) Generated by heating or photolyzing $Fe(CO)_5$.

Di- and tri-nuclear carbonylferrate ions, such as $Fe_2(CO)_8^{2-}$ and $Fe_3(CO)_{11}^{2-}$, also observed in the reaction [308], arise from the slow decomposition of $HFe(CO)_4^-$ according to the equations:

$$2HFe(CO)_4^- \rightarrow Fe_2(CO)_8^{2-} + H_2$$

$$2Fe_2(CO)_8^{2-} + H_2O \rightarrow HFe(CO)_4^- + Fe_3(CO)_{11}^{2-} + OH^- + CO$$

Although no anionic metal carbonyl carboxylate intermediate of the type indicated above has been isolated, at least one neutral species, $IrCl_2[PMe_2Ph]_2(CO)CO_2H$, prepared from $IrCl_2[PMe_2Ph]_2(CO)_2^+$ and OH^- or H_2O, has been characterized [289]. A large number of related alkoxycarbonyl- and carbamoylmetal carbonyls have also been prepared from metal carbonyl cations. Two examples of such species are π-$C_5H_5Fe(CO)_2(CO{\cdot}NMe_2)$, a carbamoylmetal carbonyl, and π-$C_5H_5Fe(CO)_2(CO{\cdot}OCH_3)$, a methoxycarbonylmetal carbonyl [290]. An investigation of the interaction between pyrrolidine and $Fe(CO)_5$ strongly suggests the presence of anionic carbamoyl species. The following scheme, entirely analogous to that presented for the interaction of hydroxide ion with $Fe(CO)_5$ was proposed to occur initially:



[291]

Carbon disulfide and, presumably, carbonyl sulfide also interact with amines and alkoxides to give, in the case of CS_2, dithiocarbamates and xanthates, an extremely important class of ligands in coordination chemistry [236] which bear an obvious resemblance to the above carbamoyliron tetracarbonyl anion.

On standing or heating, pyrollidine and a large number of oxygen and nitrogen bases, B, disproportionate $Fe(CO)_5$ to salts of the type $[FeB_m]^{2+}[Fe_n(CO)_p]^{2-}$ with m often 4 or 6 with monodentate bases and n = 1, 2, 3 or 4 when p = 4, 8, 11 or 13. The product distributions are often a sensitive function of base, temperature and other reaction conditions [8, 152]. The mechanisms by which these disproportionations occur are not well understood.

The remaining parallel reactions shown in Fig. 4. involve similar interactions of $Fe(CO)_5$ and SCO with other strong bases (CH_3^- and R_2N^-) and the thermal or photolytic cleavage of these species to give $Fe(CO)_4$ [240], presumably a diamagnetic, square planar species like other 16-electron d^8 molecules, and singlet sulfur [280]. Unfortunately, the dearth of information on the chemistry of carbonyl sulfide prevents further comparisons; however, intriguing similarities, which will not be considered here, may also be found in the much more extensively documented chemistry of carbon disulfide.

b. Comparison of the reactivity patterns of sulfur and $Fe(CO)_4$. Atomic sulfur and $Fe(CO)_4$, a primary intermediate in the thermal or photolytic decomposition of $Fe(CO)_5$ [240] are electronically equivalent species which require two electrons to achieve closed-shell configuration. They can satisfy this requirement most readily by interacting with neutral or charged Lewis bases. Several of these are shown in Fig. 5, including Ph_3P, CN^-, RNC (R = alkyl or aryl groups) and ethylene.

The chemistry of $Fe(CO)_4$ appears to have received more attention than that of atomic sulfur. In certain cases (indicated in Fig. 5) the chemical properties of atomic sulfur have been inferred from those of S_8.

The bonding in ethylene sulfide, though normally depicted as showing the ethylene group σ-bonded to the sulfur, has also been rationalized in terms of a π-interaction [317], not unlike that occurring in π-ethylenetetracarbonyliron. In the absence of a suitable donor, the $Fe(CO)_4$ group could, in principle, dimerize to form $[Fe(CO)_4]_2$, i.e.,

$$2Fe(CO)_4 \rightarrow (OC)_4Fe{=}Fe(CO)_4.$$

This reaction would be formally analogous to the dimerization of methylene to give ethylene or that of atomic sulfur to give unstable S_2, but like S=S double bonds, Fe=Fe double bonds appear to be unstable. (A bonafide S=S is evidently present in SSF_2, thiothionylfluoride [316].) Depending upon the conditions either $Fe_2(CO)_9$ and/or $Fe_3(CO)_{12}$ actually form. The latter corresponds to a trimer of $Fe(CO)_4$ and may be compared to cyclopropane which can result from the trimerization of methylene. Formally, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ may be derived from the unknown $[Fe(CO)_4]_2$ by adding CO or $Fe(CO)_4$, respectively, across the Fe=Fe double bond. However, these are formal derivations in the sense that the presence of neutral $Fe_2(CO)_8$ has not been established in photolytic or thermal reactions of $Fe(CO)_5$ [240].

A number of other photochemical reactions with $Fe(CO)_5$, presumably yielding $Fe(CO)_4$ as the initial reactive intermediate, have been investigated [240]. Metal carbonyl anions such as $Co(CO)_4^-$ and $Mn(CO)_5^-$ react with $Fe(CO)_5$ under these conditions to yield $CoFe(CO)_8^-$ and $MnFe(CO)_9^-$ which are isoelectric with $Fe_2(CO)_8^{2-}$ and $Fe_2(CO)_9$, respectively [79].

Another important way in which a carbenoid species may achieve a closed-shell configuration is by undergoing an oxidative addition reaction with another molecule. The following reactions show some representative oxidative additions:

$SnCl_2 + Cl_2 \rightarrow SnCl_4$ [318]

$Ir(CO)[PPh_3]_2Cl + H_2 \rightarrow Ir(CO)[PPh_3]_2ClH_2$ [319]

$Fe(CO)_4 + Mn_2(CO)_{10} \rightarrow Fe(CO)_4[Mn(CO)_5]_2$ [320]

In the last reaction, the actual reactant $Fe(CO)_5$ is thought to initially lose CO to form the carbenoid species $Fe(CO)_4$ which oxidatively adds the transition metal pseudohalogen $Mn_2(CO)_{10}$ at 220° C to give the product shown. Many other so-called oxidative "elimination" reactions of $Fe(CO)_5$ undoubtedly proceed by analogous initial steps. However, some coordinatively saturated d^8 complexes are sufficiently basic to cause an initial heterolytic cleavage of the added molecule. Thus:

$Os(CO)_3(PPh_3)_2 + X_2 \rightarrow [Os(CO)_3(PPh_3)_2X]^+X^-$

$[Os(CO)_3(PPh_3)_2X]^+X^- \rightarrow Os(CO)_2(PPh_3)_2X_2 + CO$ (X = Br, I) [321]

The intermediate cationic carbonyl is then susceptible to nucleophilic attack by X^-. There is evidence that the reaction of $Fe(CO)_5$ and Br_2 also proceeds, at least partially, by a similar mechanism. In this case, IR evidence for the formation of a nonionic intermediate, which may be $BrCOFe(CO)_4Br$, has also been presented [322]. Such heterolytic cleavages or related concerted processes are probably important whenever $Fe(CO)_5$ undergoes oxidative elimination in the absence of light at low temperatures, since under these conditions $Fe(CO)_4$ is unlikely to form as a discrete intermediate. For example, $Fe(CO)_5$ does not become an active hydrogenation catalyst until ca. 160° C [323]. It seems likely that only at or above this temperature does sufficient active catalyst (i.e., $Fe(CO)_4$) form to permit rapid oxidative addition of hydrogen [324].

3. *Preparation and chemistry of* $Ru(CO)_4^{2-}$ *and* $Os(CO)_4^{2-}$.

The reduction of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ by sodium in liquid ammonia is reported to give pale yellow ruthenium [393] or cream osmium [394] products, respectively. These solids have not been characterized but behave as if they are $Na_2M(CO)_4$, $NaHM(CO)_4$, $Na_2M_2(CO)_8$, or a mixture thereof. Reactions of the osmium species are shown in Fig. 6. In contrast to $Na_2Fe(CO)_4$ and the aforementioned "pale yellow ruthenium solid", (both pyrophoric materials) the cream osmium solid is reportedly air-stable. Further, in the presence of an aqueous solution of $[Ni(bipy)_3]Cl_2$ the cream solid gives a product of composition $[Ni(bipy)_3][Os(CO)_4]_2$ and in a THF solution many of its bands are attributable to $NaHOs(CO)_4$ which has been prepared previously by sodium sand reduction of $H_2Os(CO)_4$ in THF [396].

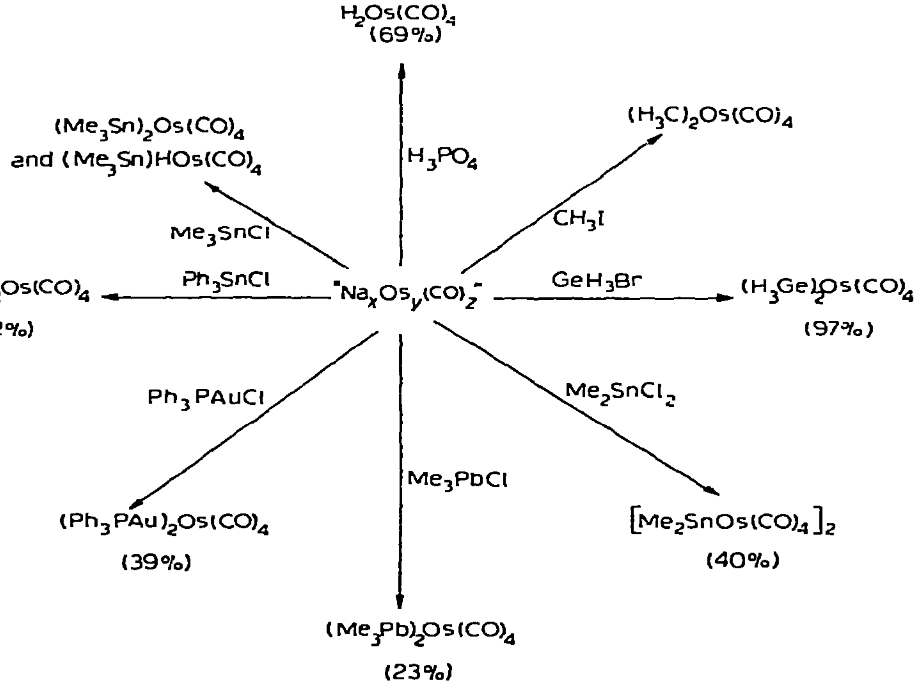


Fig. 6. Reactions of cream solid isolated from sodium reduction of $Os_3(CO)_{12}$ in ammonia (all data from ref. 394, yield in parentheses.) The cream solid has not been characterized (see text).

Similar ruthenium species are obtained by treating the pale yellow ruthenium solid with electrophilic reagents. Yields of the products, however, are generally far lower than those from corresponding osmium reactions. For example, (yields in parentheses): $H_2Ru(CO)_4$ (25%) [395], *cis*-$(Me_3Sn)_2Ru(CO)_4$ (33%) [393], *trans*-$(Ph_3Sn)_2Ru(CO)_4$ (6%) [393], *trans*-$[(PhCH_2)_3Sn]_2Ru(CO)_4$ (9%) [393] and *cis*-$(Me_3Pb)_2Ru(CO)_4$ (trace) [393].

B. Pentacarbonylmetallates of Cr, Mo and W

1. Preparation

Pentacarbonylmetallate dianions of Cr, Mo and W were first obtained by alkali metal reductions of the corresponding hexacarbonyls in liquid ammonia [310]. No yields were reported but the Mo and W compounds were more difficult to obtain pure by this method than the chromium salt. Subsequently, it was shown that purer samples of yellow $Na_2Mo(CO)_5$ [311] and $Na_2W(CO)_5$ [312] may be prepared by the disproportionation of $Na_2M_2(CO)_{10}$ (M = Cr, Mo, W) in a sealed tube containing carbon monoxide at 130-150° C according to the equation:

$$Na_2M_2(CO)_{10} + CO \rightarrow Na_2M(CO)_5 + M(CO)_6$$

The pentacarbonylmetallates are freed from the hexacarbonyls by simple sublimation. However, at least in the case of tungsten, sublimations at temperatures above 70° C result in CO evolution approximately in accord with the equation:

$$2Na_2W(CO)_5 \rightarrow Na_4W_2(CO)_9 + CO \qquad [312]$$

The existence of $Na_4W_2(CO)_9$ is uncertain as its formulation is based only on gas volumetric studies. Also, attempts to repeat a preparation [346] of $Cs_4Cr_2(CO)_9$ gave instead $Cs_2Cr(CO)_5$ [342]. The previously reported spectrum of $Cs_4Cr_2(CO)_9$ [346] in hexamethylphosphoramide was found to be very similar to that of a mixture of $Cs_2Cr_2(CO)_{10}$ and $Cs_2Cr(CO)_5$ [342]. In the alkali metal reduction of $Cr(CO)_6$ and the other Group VI hexacarbonyls in liquid ammonia approximately 90-95% of the liberated carbon monoxide is reduced to a shock-sensitive substance known as "sodium carbonyl" of composition $(NaCO)_x$, which has been recently recognized to contain disodium acetylenediolate [357]. A minimum of about three equivalents of sodium is thus required to ensure complete reduction of $Cr(CO)_6$ to $Cr(CO)_5^{2-}$ in liquid ammonia.

$$Cr(CO)_6 + 3Na \xrightarrow{NH_3} Na_2Cr(CO)_5 + 1/2[Na_2(CO)_2]$$

An improved preparation of $Na_2Cr(CO)_5$ has been recently published in which this explosive byproduct is removed by filtration of the liquid ammonia solution. Evaporation of the resulting clear orange solution gives an 85% yield of light yellow $Na_2Cr(CO)_5$ [313].

In a recent development nearly quantitative yields of $M(CO)_5^{2-}$ (M = Cr, Mo and W) have been obtained by alkali metal reductions of $M(CO)_6$, $M_2(CO)_{10}^{2-}$ and $M(CO)_5X^-$ (X = Cl, Br and I) in hexamethylphosphoramide [342].

Cesium amalgam reductions of $M(CO)_6$ in tetrahydrofuran also give excellent yields of $M(CO)_5^{2-}$ [314]. Other reported preparations of $Cr(CO)_5^{2-}$ include a high-pressure reductive carbonylation of $CrCl_3$ in diglyme above

100° C [424] and the reduction of $Cr(CO)_6$ by sodium amalgam in refluxing tetrahydrofuran [424]. The latter reaction has been subsequently shown by infrared studies to be incomplete after 12 hours. A substantial amount of the intermediate, $Cr_2(CO)_{10}^{2-}$, remains unreduced [314]. Analogous reductions of $Mo(CO)_6$ and $W(CO)_6$ with Na or K/Hg produce only poor yields of the corresponding monomeric dianions, possibly because these species are unstable in THF.

2. *Chemistry of* $M(CO)_5^{2-}$

The chemistry of the Group VI monomeric dianions has received much less attention then that of $Fe(CO)_4^{2-}$, principally because of their relative inaccessibility. Until recently [314] pure samples of salts of $Mo(CO)_5^{2-}$ and $W(CO)_5^{2-}$ were available only from the thermal disproportionation of the corresponding $M_2(CO)_{10}^{2-}$. This reaction is technically difficult and yields only small amounts of products. Consequently, only the chemistry of $Na_2Cr(CO)_5$ has been examined in any detail. Table 4 shows a compilation of reactions of $Cr(CO)_5^{2-}$ that have been reported thru 1973. The reactivity patterns of $Fe(CO)_4^{2-}$ and $Cr(CO)_5^{2-}$ appear to be similar; however, the latter is a substantially stronger reducing agent. Thus, in air-free water $Cr(CO)_5^{2-}$ is oxidized to the binuclear hydride, $HCr_2(CO)_{10}^-$ [325]:

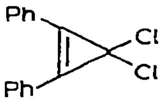
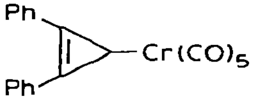
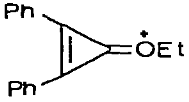
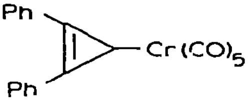
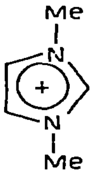
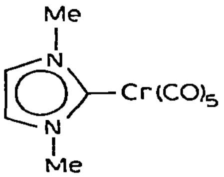
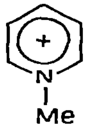
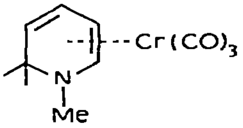
$$2Cr(CO)_5^{2-} + 3H_2O \rightarrow HCr_2(CO)_{10}^- + H_2 + 3OH^-$$

In the presence of aqueous ferroin, $Fe(o\text{-phen})_3Cl_2$, however, an insoluble salt of the monoprotonated dianion, $Fe(o\text{-phen})_3[HCr(CO)_5]_2$, is reportedly obtained [325]. The salt has been characterized only by elemental analysis; however, methylpyridinium [335] and 1,3-dimethylimidazolium [334] salts containing this anion have also been reported. Similarly, the action of an aqueous solution of Me_4NI on $W(CO)_5^{2-}$ yields $[Me_4N][HW(CO)_5]$ [312]. No salts containing $HMo(CO)_5^-$ are known. An early report on the formation of $H_2Cr(CO)_5$ [336] has been shown to be invalid [337]. Attempts to acidify an ethereal solution of $Cr(CO)_5^{2-}$ lead to the formation of a nonvolatile species, probably $[Et_2OH][HCr(CO)_5]$ or $[Et_2OH][HCr_2(CO)_{10}]$ [325]. The latter is the salt of a strong acid [102]. It is possible that $HCr(CO)_5^-$ would also be a salt of a strong acid in view of the reluctance of chromium to become seven coordinate.

Nitrogen bases, such as pyridine, *ortho*-phenanthroline and ethylenediamine, in aqueous media oxidize $Cr(CO)_5^{2-}$ to neutral substituted carbonyls as shown in Table 4. The binuclear hydride, $HCr_2(CO)_{10}^-$, also forms in this reaction. The remaining reactions of $Cr(CO)_5^{2-}$ are more characteristic of those of $Fe(CO)_4^{2-}$. Thus, $Cr(CO)_5^{2-}$ reacts with $Fe(CO)_5$ and $M(CO)_6$ (M = Cr, Mo and W) in ethereal solvents to give mixed-metal carbonyl anions, $CrFe(CO)_9^{2-}$ and $CrM(CO)_{10}^{2-}$ [313], which are completely analogous to $MnFe(CO)_9^-$ and $MnM(CO)_{10}^-$. The latter are obtained by a similar treatment of isoelectronic $Mn(CO)_5^-$ with $Fe(CO)_5$ [79] or $M(CO)_6$ [339], respectively. A few halide displacement reactions with $Cr(CO)_5^{2-}$ are also known. Low yields of π-cyclobutadienetetracarbonylchromium are obtained by treating $Na_2Cr(CO)_5$ in THF with dichlorocyclobutenes [330]. Analogous molybdenum and tungsten derivatives have also been prepared in 35 and 1% yields, respectively. In these reactions the "$Mo(CO)_5^{2-}$" was prepared by reduction of $Mo(CO)_6$ by sodium in either liquid ammonia or refluxing

TABLE 4

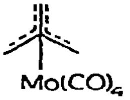
REACTIONS OF $Cr(CO)_5^{2-}$ AND $HCr(CO)_5^-$

Reactant	Principal product(s)	Reference
NH_4Cl in NH_3	$Cr(CO)_5NH_3$	325
pyridine in H_2O	$Cr(CO)_5py$	325
o-phen in H_2O	$Cr(CO)_4(o\text{-phen})$	325
en in H_2O	$Cr(CO)_4en$	325
$Fe(o\text{-phen})_3Cl_2$ in H_2O	$[Fe(o\text{-phen})_3][HCr(CO)_5]_2$	325
H_2O	$HCr_2(CO)_{10}^-$	325
aniline in H_2O	$Cr(CO)_5$ aniline	327
CN^- in H_2O	$Cr(CO)_5CN^-$ and $Cr(CO)_4(CN)_2^{2-}$	326
X_2 (X = I, CN) in ether	$Cr(CO)_5X^- + X^-$	328
$Fe(CO)_4I_2$	$Cr(CO)_5I^- + Fe(CO)_4I^-$	329
$Fe(CO)_5$	$[Cr(CO)_5Fe(CO)_4]^{2-}$	313
$M(CO)_6$ (M = Cr, Mo, W)	$[Cr(CO)_5M(CO)_5]^{2-}$	313
3,4-dichlorocyclobutene	$\pi\text{-}C_4H_4Cr(CO)_4$ (low yield)	330
Me_2NCHCl_2	$Me_2NCHCr(CO)_5$	274
	 (19.5% yield)	331
		332
 $[HCr(CO)_5]^-$		334
 $[HCr(CO)_5]^-$	 (80% yield)	335
Ph_3MCl (M = Ge, Sn, Pb)	$Ph_3MCr(CO)_5^-$	342
$C_5H_5Fe(CO)_2I$	$C_5H_5FeCr(CO)_5^-$	342
Me_3SnCl	$Me_3SnCr(CO)_5^-$	342
Cl_2CS	$(OC)_5CrCS$	362

tetrahydrofuran. Although the latter method gave higher yields of $\pi\text{-}C_4H_4Mo(CO)_4$ (up to 35%), the authors did not determine whether the low yields in certain reacions were due to initial poor yields of monomeric dianions or to other reasons [330]. Since they did not establish that the monomeric dianions were the reacting species, it cannot be ruled out that dimeric dianions which also form in the above reductions were in fact the metal reactants. In the latter case $ClM(CO)_5^-$ would also be a product. Similar reactions of these dimeric dianions with Group IV dihalides are known [340] and proceed according to the following equation:

$$R_2M'Cl_2 + Na_2Cr_2(CO)_{10} + THF \rightarrow \underset{\underset{THF}{\uparrow}}{R_2M'Cr(CO)_5} + NaCl + NaCr(CO)_5Cl$$

The reaction of 3-chloro-2-(chloromethyl)propene with "$Mo(CO)_5^{2-}$", generated from $Mo(CO)_6$ and Na in THF, gave π-trimethylenemethanetetracarbonylmolybdenum (V) in 1% yield in addition to the novel species (VI) in 2% yield [299]. Again, it is possible that $Mo_2(CO)_{10}^{2-}$ or some carbonyl anion other than $Mo(CO)_5^{2-}$ is the actual metal reactant in this system.

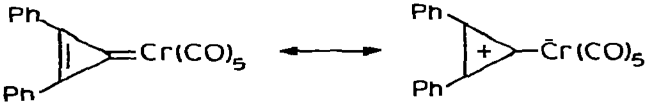


(V)

(VI)

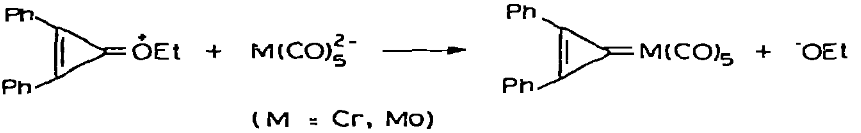
Tungsten and chromium analogues of A or B could not be obtained by the above method.

Two pentacarbonylcarbenechromium species have been obtained by treating $Cr(CO)_5^{2-}$ with geminal dihalides. The first utilization of this potentially important general route to carbenes was reported in 1967 in the preparation of VII [331].



(VII)

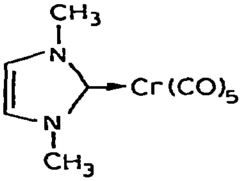
Recently, the same substance, in addition to its molybdenum analogue, has been prepared in nearly quantitative yields by reaction of the monomeric dianions in accord with the equation:



[332]

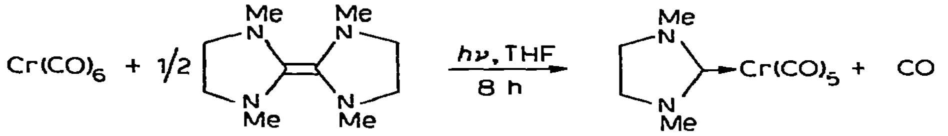
The source of $M(CO)_5^{2-}$ in the above report was not indicated.

Another pentacarbonylcarbenechromium species, VIII, was formed by heating 1,3-dimethylimidazolium hydrogen pentacarbonylchromate at 120° in high vacuum [334].



(VIII)

A saturated analogue of VIII was obtained by the following route:



[341]

Interactions of $Ph_3M'Cl$ (M = Ge, Sn, Pb) with $M(CO)_5^{2-}$ (M = Cr, Mo and W) have been shown to give air-stable, colorless salts of the type $Ph_3M'M(CO)_5^-$. The tin derivatives are also obtained by the room temperature reaction of $Ph_3Sn:^-$ with $M(CO)_6$ in THF. Other halides such as Me_3SnCl and $C_5H_5Fe(CO)_2I$ interact with $Cr(CO)_5^{2-}$ to yield $C_5H_5Fe(CO)_5^-$ and $Me_3SnCr(CO)_5^-$, respectively [342].

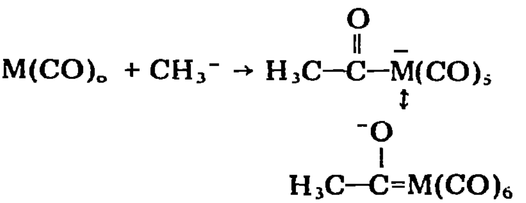
Thiocarbonyl complexes have also been prepared from $M_2(CO)_{10}^{2-}$ and/or $M(CO)_5^{2-}$ (mixture of anions prepared by the sodium amalgam reduction of $M(CO)_6$ in refluxing THF) and thiophosgene [362]. As in the case of other reactions [330, 333], the identity of the actual metal reactant(s) remains obscure.

3. The chemistry of some derivatives of $M(CO)_5^{2-}$

Since the $M(CO)_5$ units, where M = Cr, Mo and W, like $Fe(CO)_4$, are electronically equivalent to a chalcogen atom, they form a variety of derivatives which have stoichiometries and reactivity patterns similar to those of chalcogen analogues. For example, it is found that $M(CO)_6$, $(RO)R'CM(CO)_5$, an alkoxycarbene derivative, and to a lesser extent $M_2(CO)_{10}^{2-}$ have reactivity patterns which are similar, in many cases, to those of SCO, (RO)R'CS, a thione ester, and S_2^{2-}, respectively. The chemistry of $M(CO)_6$ parallels that of $Fe(CO)_5$ which was described earlier. In the reaction of a Lewis base with $M(CO)_6$, the first step is generally the formation of a coordinatively unsaturated, carbenoid $M(CO)_5$ species [367]. Strong bases, however, often attack a coordinated carbonyl group at low temperature to give an acyl carbonyl species. Examples of these two principal reactivity patterns are given below in equation form and bear an obvious resemblance to those of SCO (cf. Fig. 4).

$$M(CO)_6 \xrightarrow{\Delta\ \text{or}\ h\nu} M(CO)_5 + CO \xrightarrow{B} M(CO)_5B$$

where B = Ph_3P, NH_3, Cl^-, $Mn(CO)_5^-$, etc.



$$M(CO)_6 + CH_3^- \rightarrow H_3C{-}\overset{\overset{\large O}{\|}}{C}{-}\overline{M}(CO)_5 \;\updownarrow\; H_3C{-}\overset{\overset{\large ^-O}{|}}{C}{=}M(CO)_6$$

Recent reviews [8, 152, 358] have described the chemistry of $M(CO)_6$ in detail, therefore it will not be considered here further. However, no such detailed accounts of the chemistry of the Group VI dimeric dianions exist, nor have recent reviews on transition metal carbenes [147, 360] emphasized the similarities, first recognized by Fischer and coworkers [361], in the chemistry of the carbenepentacarbonylmetal species and organic esters. Accordingly, the chemistry of these two classes of metal carbonyl compounds will now be discussed, where possible, with respect to that of their main group analogues.

a. The decacarbonyldimetallate dianions of Cr, Mo and W. Two reliable methods for the preparation of the Group VI dimeric dianions have been developed and involve the reduction of $M(CO)_6$, M = Cr, Mo, W, either by sodium amalgam in THF in the presence of UV radiation [102] or by excess sodium in the presence of catalytic amounts of 2,2'-bipyridyl in THF [363]. Controlled aerial oxidation of solutions of $M(CO)_5{}^{2-}$ also gives essentially quantitative yields of $M_2(CO)_{10}{}^{2-}$ [342].

Bis(triphenylphosphine)iminium (PPN^+) salts of these and other carbonyl anions, which are remarkably air-stable in solution and in the solid state, have been prepared [364]. The crystal structure of $(PPN)_2Cr_2(CO)_{10} \cdot CH_2Cl_2$ has been determined and shows the $Cr_2(CO)_{10}{}^{2-}$ unit to be essentially isostructural with the isoelectronic $Mn_2(CO)_{10}$ [365]. A comprehensive summary of the reactions of $Cr_2(CO)_{10}{}^{2-}$ thru 1973 is depicted in Fig. 7 and 8. In most cases the corresponding molybdenum and tungsten salts react to give analogous products; however, the molybdenum analogue often gives less stable and/or tractable products. While the tungsten dimer often gives products which are more thermally and oxidatively stable than the chromium analogues, in certain cases it appears to be much less reactive than the chromium dianion. For example, the tungsten dimer is reported not to react with mercury metal [345]. One outstanding feature in the chemistry of these dianions is their substantially greater reactivity compared to the isoelectronic neutral decacarbonyls of manganese, technetium and rhenium. This enhanced reactivity is undoubtedly due in part to the weaker M—M bonds in the dianions which result, at least partially, because the adjacent metals in these species bear negative charge. Thus, although SnI_2 inserts into the Cr—Cr bond in $Cr_2(CO)_{10}{}^{2-}$ at room temperature in THF to give $[(CO)_5CrSnI_2$-

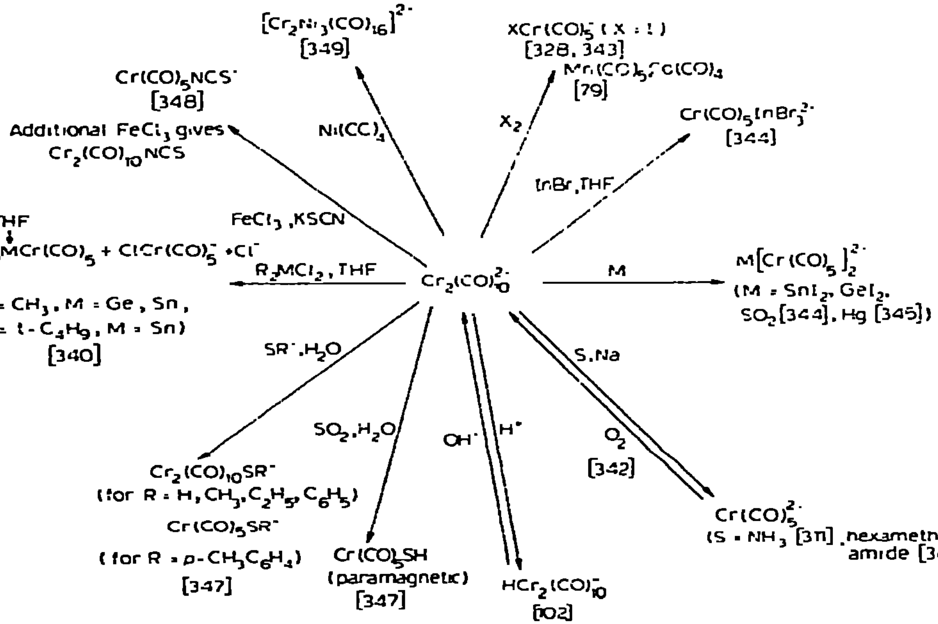


Fig. 7. Reactions of $Cr_2(CO)_{10}{}^{2-}$ with various reagents (references in brackets).

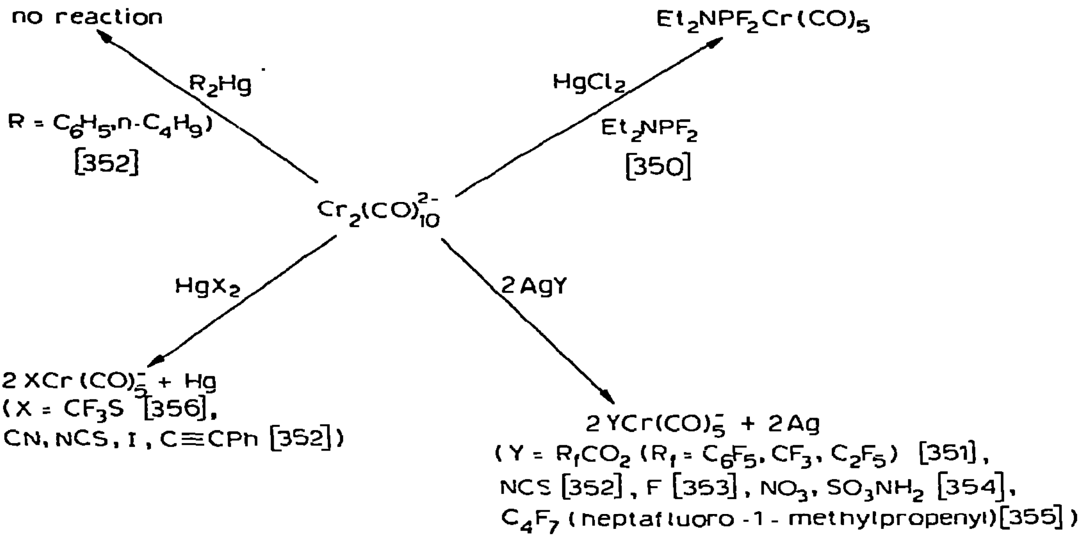
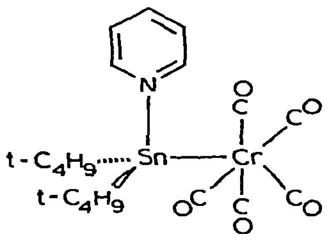


Fig. 8. Reactions of $Cr(CO)_{10}^{2-}$ with HgX_2 and AgX. (references in brackets).

$Cr(CO)_5]^{2-}$ [344], only under forcing conditions (180-190°, sealed tube) does $Mn_2(CO)_{10}$ undergo similar insertions [368]. The only other reactions in Fig. 6 and 7 demonstrated for $Mn_2(CO)_{10}$ include that with I_2 to give $IMn(CO)_5$ [8], H^+ to give $HMn_2(CO)_{10}^+$ [150] and Na reduction to give $Mn(CO)_5^-$ [8].

A significant departure in the chemistries of $Cr_2(CO)_{10}^{2-}$ and $Mn_2(CO)_{10}$ occurs in their respective interactions with InBr. While $Mn_2(CO)_{10}$ gives the expected insertion product $InBr[Mn(CO)_5]_2$ [368], $Cr_2(CO)_{10}^{2-}$ forms $Cr(CO)_5$-$InBr_3^{2-}$ [344], which may be regarded as an adduct of $Cr(CO)_5^{2-}$ and $InBr_3$.

It is noteworthy that $InBr_3$ and $Fe(CO)_4^{2-}$ give rise to an analogous product, $Fe(CO)_4InBr_3^{2-}$ [34]. Metallic indium and small amounts of $Cr(CO)_5Br^-$ are reported to be formed in the chromium reaction, however, the equation shown for the reaction in the original paper [344] is not charge-balanced. The formation of some other species, such as $Cr(CO)_5THF$, must be invoked to explain the formation of metallic indium. One of the more novel reactions shown in Fig. 7 is that of $Cr_2(CO)_{10}^{2-}$ with R_2MCl_2, giving THF or other base-stabilized dialkyl stannylenes or germylenes coordinated to a $Cr(CO)_5$ unit. The other products are $ClCr(CO)_5^-$ and free chloride ion [340]. The crystal structure of one of these, $(t\text{-}C_4H_9)_2SnCr(CO)_5 \cdot C_5H_5N$, has been determined [370], the essential features of which are shown below.



Recently, a base-free stannylene has been prepared by the following reaction [371]:

$M(CO)_6 + R_2Sn \rightarrow R_2SnM(CO)_5$

$(M = Cr, Mo; R = (Me_2Si)_2CH)$

The reaction of nickel tetracarbonyl with $M_2(CO)_{10}^{2-}$ gives rise to a polynuclear carbonyl anion of stoichiometry $M_2Ni_3(CO)_{10}^{2-}$. The structures of the bis(triphenylphosphine)iminium salts of the Cr, Mo and W species have been determined [349] and show these ions to contain a trigonal bipyramidal cluster of metal atoms with the nickels occupying the equatorial positions and $M(CO)_5$ units in the axial positions. The use of $(Et_4N)_2Mo_2(CO)_{10}$, instead of $(PPN)_2Mo_2(CO)_{10}$, in the $Ni(CO)_4$ reaction gives another cluster compound $(Et_4N)_2[Mo_2Ni_4(CO)_{14}]$. The details of the structure of this substance are presently available only in preliminary form [349].

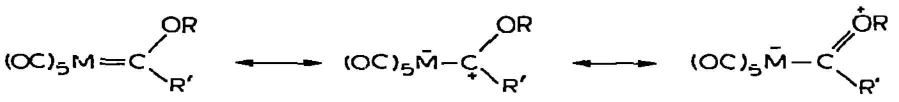
Oxidation of $Cr_2(CO)_{10}^{2-}$ by $FeCl_3$ on the presence of KSCN yields $Cr(CO)_5SCN^-$; paramagnetic $Cr_2(CO)_{10}NCS$ is obtained with additional $FeCl_3$ [348]. Aqueous solutions of mercaptide ions and sulfur dioxide give species of the type $Cr_2(CO)_{10}SR^-$ and paramagnetic $Cr(CO)_5SH$ [347]. Undoubtedly the most interesting and synthetically useful reactions of the dimeric dianions are represented in Fig. 8. All of these investigations have been carried out by Ruff and coworkers and involve the general reactions:

$HgX_2 + M_2(CO)_{10}^{2-} \rightarrow 2XM(CO)_5^- + Hg$

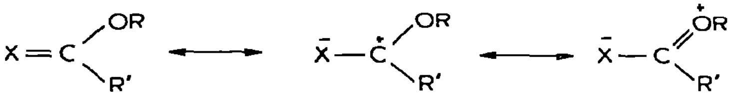
$2AgX + M_2(CO)_{10}^{2-} \rightarrow 2XM(CO)_5^- + 2Ag$

The nature of X has ranged from the heptafluoro-1-methylpropenyl group which gives $C_4F_7M(CO)_5^-$ (M = Cr, Mo, W) [355] to a fluorine atom to give the first well-characterized fluorocarbonylmetallates (M = Cr, W) [353]. The latter were also prepared by photolyzing methylene chloride solutions of $M(CO)_6$ and $[PPN]F \cdot CH_2Cl_2$. Other X groups include Cl, I, Br, R_fCO_2 where R_f = perfluoroalkyl and -aryl groups, SCN, NO_3, SCF_3, SO_3NH_2, CN and $C{\equiv}CPh$. For references see Fig. 8. Dialkyl- and diaryl-mercury compounds did not react with $M_2(CO)_{10}^{2-}$ [352], thus precluding the use of this reaction as a pathway to presently unknown (R, Ar) $M(CO)_5^-$ species. Since $M(CO)_5$ units are electronically equivalent with the sulfur atom, in principle, it should be useful to compare the reactivity patterns of $M_2(CO)_{10}^{2-}$ with those of the disulfide dianion. Unfortunately, so little appears to be known about the chemistry of S_2^{2-} [366] that an objective comparison is impossible. There do exist numerous derivations of S_2^{2-} of the type Y_2S_2, where Y = H, Cl, alkyl or aryl groups, that have no Group VIb analogues presently (but $Fe(CO)_4$ analogues exist for some, see Table 3); however, undoubtedly, many of these are capable of existence. A significant difference in the chemistry of these transition metal species compared to their main group analogues involves the former's ability to utilize various X groups as bridging ligands. Thus, although $HCr_2(CO)_{10}^-$ is stoichiometrically related to HS_2^-, the former contains a hydrogen atom bridging two $Cr(CO)_5$ units [365], whereas the latter presumably contains a normal HSS^- grouping. Other related bridged dinuclear carbonyl anions include $Cr_2(CO)_{10}X^-$ (X = I, Br, Cl, CN, SCN and RS) [369]. No disulfide analogues of these bridged species are known.

b. Comparison of pentacarbonylcarbenemetal(0) and organic ester chemistry. Complexes of the type M(COR)R′ where M = $M(CO)_5$ [372] (M = Cr, Mo, W) or other metal carbonyl groups [360] have been regarded as metal-stabilized carbene [372], carboxonium [373] or ylide [374] species depending on which of the following resonance forms of the carbene hybrid are regarded as most significant.

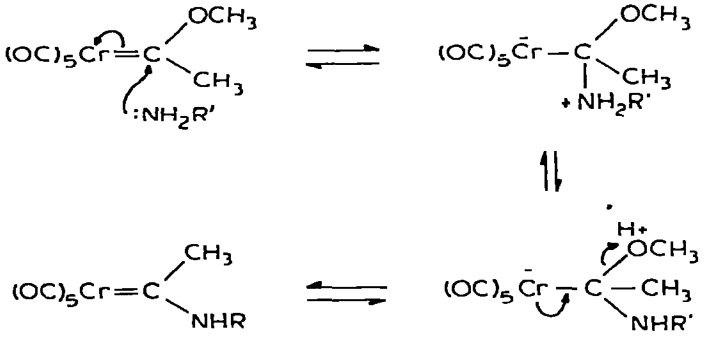


Fischer and coworkers have noted striking similarities in the structures and reactivity patterns of metal carbenes and organic esters. For example, the X-ray crystal structure of pentacarbonylphenylmethoxycarbenetungsten shows that the carbene moiety in this species closely resembles that of methyl benzoate [375]. The ability of these metal carbenes to undergo aminolysis, base addition and base exchange reactions is also in accord with their ester-like behavior. Resonance forms similar to the preceding have been invoked to account for the chemical properties of organic esters, i.e.,



(X = O, S)

Since $M(CO)_5$ units are electronically equivalent to an oxygen or sulfur atom, such a correspondence should not be surprising. Figure 9 shows a variety of reactions of pentacarbonylcarbene complexes of Cr, Mo and W which are analogous to reactions of organic esters with the same or similar reagents. The aminolysis reaction has been carefully studied and it appears that the mechanism for incorporation of a NHR′ group is remarkably similar to that of a corresponding ester reaction [361]; i.e.,



Triethylphosphine has been shown to react with $Cr(CO)_5C(OCH_3)CH_3$ at −20° to form the isolable phosphorus ylide (IX) [380] which is analogous to the labile nitrogen ylide intermediate in the aminolysis mechanism. A similar thermally unstable nitrogen ylide has recently been isolated [383].

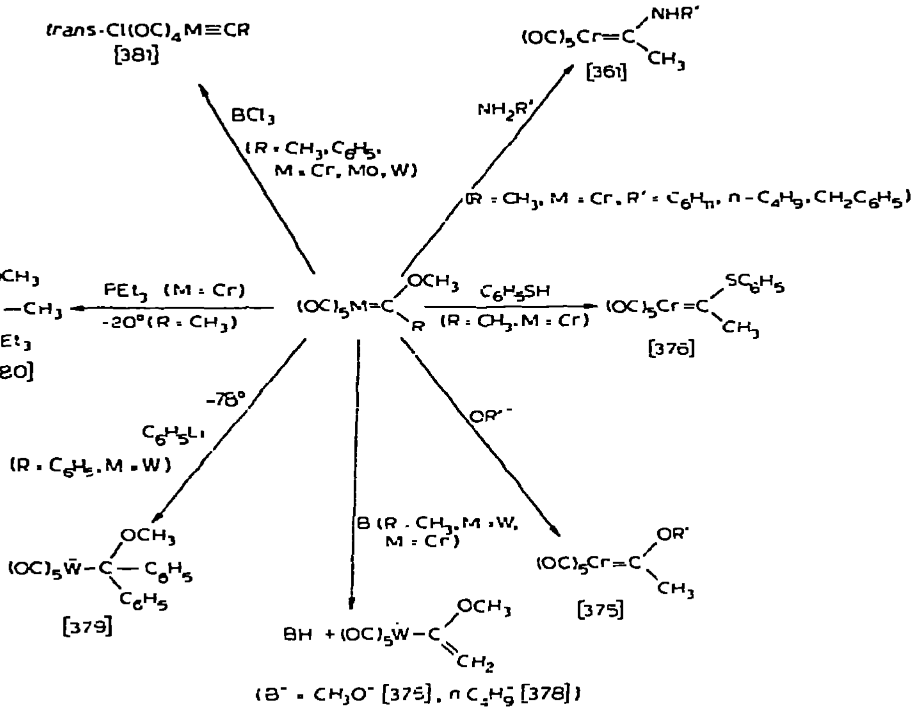
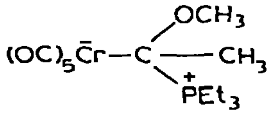


Fig. 9. Chemistry of metal carbenes. organometallic analogues of organic esters (references in brackets).

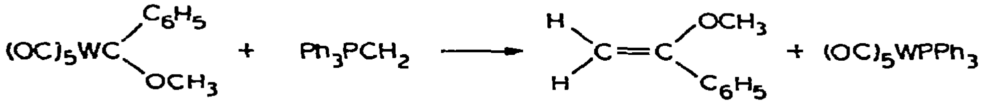


(IX)

The addition of phenyllithium to pentacarbonylphenylmethoxycarbenetungsten at −78° is proposed to give a similar species containing a tetrahedral carbon (see Fig. 9). Treatment of this species at −78° C with HCl gives a 50% yield of $(OC)_5WCPh_2$, one of the very few known transition metal carbenes not containing a donor heteroatom α to the carbene carbon. Methylenetriphenylphosphorane interacts with $(OC)_5WCPh_2$ to give products analogous to those obtained with benzophenone; i.e.,

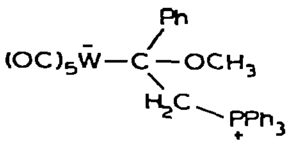
$$(OC)_5WCPh_2 + Ph_3PCH_2 \rightarrow (OC)_5WPPh_3 + H_2C{=}CPh_2$$

Nearly a quantitative yield of 1,1-diphenylethylene is obtained [379]. The latter reaction also proceeds analogously with the ester-like carbene complexes [374], e.g.,



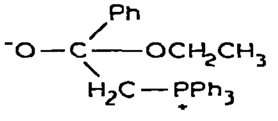
The high yields of vinyl ethers obtained from this reaction (82% in above example) suggest that the method may be a synthetically useful route to these species.

A betaine-like intermediate (X) was proposed to form via an initial nucleophilic attack of the Wittig reagent with the carbene complex.

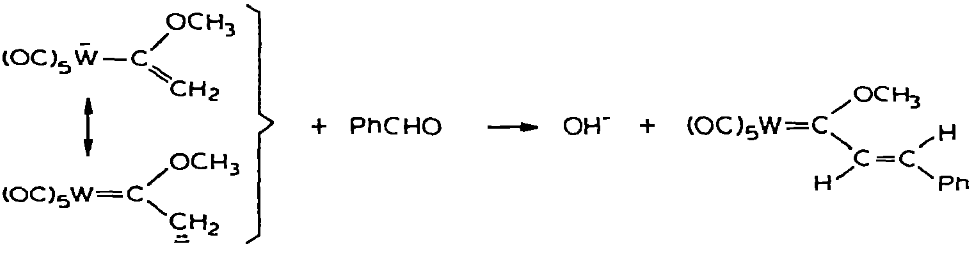


(X)

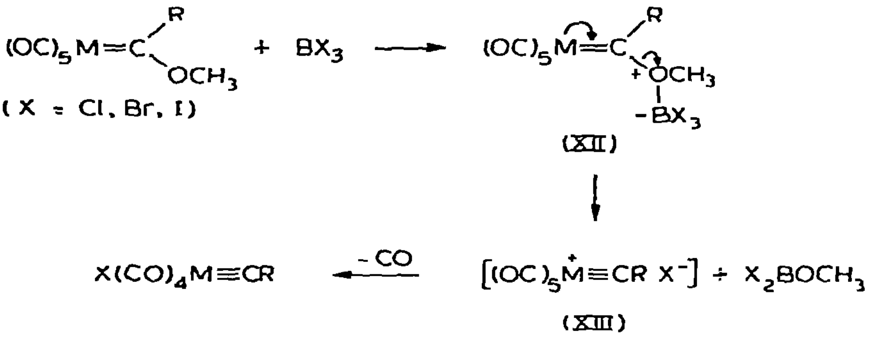
An entirely analogous intermediate (XI) has been suggested to form in the reaction of Ph_3PCH_2 with ethylbenzoate [382]. However, in this case, the intermediate eliminates an ethoxide ion giving the salt $Ph_3\overset{+}{P}CH_2COPhOEt^-$. Subsequently, the anion abstracts an α hydrogen forming ethanol and $Ph_3PCHCOPh$ instead of the vinyl ether. Undoubtedly, the $W(CO)_5$ unit is not as effective as oxygen in causing such elimination reactions. Sulfur should also be less effective than oxygen in this regard; however, the interaction of Wittig reagents with the less accessible thione esters has apparently not been investigated. As in the case of esters, α hydrogens in carbene complexes of the type (RO)R′CM are readily exchanged in the presence of base [375]. New carbene complexes have been synthesized by the abstraction of an α proton and subsequent reaction of the resultant stabilized carbanion with an electrophile [378], e.g.,



(XI)



Recently, alkoxycarbene complexes have been found to react with boron trihalides to give species which may formally be considered carbyne complexes. An X-ray crystallographic determination of the structure of one of these species, *trans*-$C_6H_5CW(CO)_4I$, formed in the reaction of BI_3 with $(CH_3O)C_6H_5W(CO)_5$, shows an abnormally short W—C(carbyne) bond which is suggested to correspond to a W—C triple bond [381]. Although no mechanism for the formation of these carbyne complexes has been suggested, an initial electrophilic attack of the boron trihalide on the alkoxy oxygen to give zwitterion XII is likely. In accord with the analogy between organic esters and alkoxy carbenes, the next step would be the formation of a carbonyl cation (XIII, analogous to an acylium ion) which is attacked by halide to give the observed product, i.e.,



Acylium ions, R—C≡$\overset{+}{O}$, are believed to form by a similar mechanism in the reaction of organic esters and carboxylic acids with Lewis acids and concentrated sulfuric acid [384].

C. Tricarbonylmetallates of nickel, palladium and platinum

These species are known only in the form of derivatives such as $Ni_2(CO)_6^{2-}$ [8, 385], $Ni(CO)_3I^-$ [386], and $Ni(CO)_3GeCl_3^-$ [387]. No corresponding platinum or palladium derivatives are known although crystal structures of related cluster species $[Pt_3(CO)_3(\mu\text{-}CO)_3]_n^{2-}$ ($n = 2, 3, 4, 5$) have been reported [388]. Nickel analogues of these clusters are also known [389].

D. Cyclopentadienylcarbonylmetallate dianions

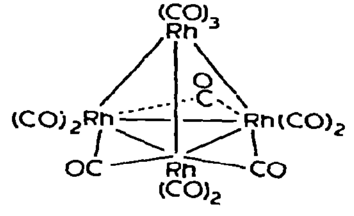
The only known cyclopentadienyl substituted carbonylmetallate dianion is $C_5H_5V(CO)_3^{2-}$, prepared by treating $C_5H_5V(CO)_4$ with 1% sodium amalgam in THF [262, 391]. Treatment of this dianion with 2*N* HCl in ether yields the unusual coordinatively unsaturated species (each vanadium formally has 16 valence electrons) $(C_5H_5)_2V_2(CO)_5$ whose structure has been recently determined by X-ray crystallography [392]. No other chemistry of this dianion has been reported.

IV. Carbonyl trianions

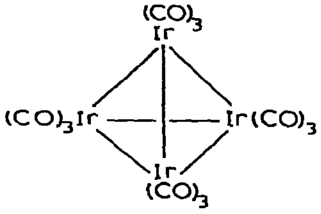
Transition metal groups such as $Co(CO)_3$, $Mn(CO)_4$, $V(CO)_5$, π-$C_5H_5Fe(CO)$, π-$C_5H_5Cr(CO)_2$, etc. are 15-electron species and electronically equivalent to Group Va atoms which comprise the pnicogen family of elements. In principle, these transition metal "pseudopnicogen" groups could form trianions analogous to those of the main group elements. Although such species are presently unknown, they do exist in the form of neutral derivatives which will now be discussed.

A. Derivatives of $M(CO)_3^{3-}$ (M = Co, Rh, Ir)

The best known 15-electron species is tricarbonylcobalt which may be isolated as a tetramer, $[Co(CO)_3]_4$ [152] and which consists of a tetrahedral array of cobalt atoms (cf. structure XIV). In this manner each cobalt thereby attains a closed-shell configuration just as phosphorus, arsenic or antimony do in forming P_4, As_4 or Sb_4, respectively. Similarly, tricarbonylrhodium and tricarbonyliridium are isolated as tetramers, $[M(CO)_3]_4$ (M = Rh, Ir). The cobalt and rhodium species XIV contain 3 bridging carbonyl groups while $Ir_3(CO)_{12}$ (XV) possesses only terminal carbonyls, having a structure strictly analogous to that of the molecular forms of P, As and Sb.

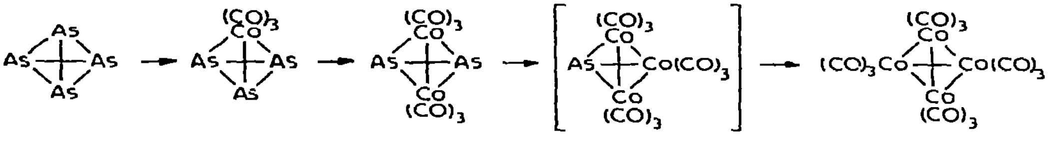


(XIV)



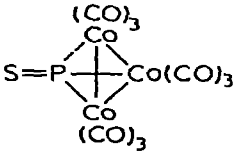
(XV)

The most dramatic demonstration of the pseudopnicogen character of the $Co(CO)_3$ group is its ability to formally replace one or more arsenic or phosphorus atoms in As_4 or P_4 while preserving the basic tetrahedral structure of the molecule. Such a formal replacement scheme is shown below, where XX has three bridging carbonyl groups (cf. structure XIV). Only compound XIX is presently



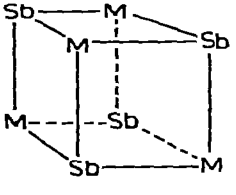
(XVI)[397] (XVII)[7] (XVIII)[399] (XIX) (XX)[152]

unknown, however, a phosphorous sulfide analogue $Co_3(CO)_9PS$ (XXI) [400] has been prepared in addition to a large number of other compounds of stoichiometry $RECo_3(CO)_9$ where R = H, Cl, alkyl, aryl, etc. for E = C [401] and R = C_6H_5 for E = Ge [44]. The phosphorus analogue of XVIII, $P_2Co_2(CO)_6$ has also been reported [400]. Attempts to prepare $Sb_2Co_2(CO)_6$ led instead



(XXI) [400]

to a novel tetrameric species $Sb_4Co_4(CO)_{12}$ which has a cubic framework, XXII [402], corresponding to a derivative of unknown Sb_8. In addition to mixed main-group transition metal species, corresponding Rh—Co compounds are known, including $Co_3Rh(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, and $CoRh_3(CO)_{12}$ [403].



(XXII) (M = Co(CO)$_3$)

TABLE 5

SUMMARY OF SYNTHETIC METHODS FOR THE PREPARATION OF TETRAMERS OF THE TYPE $R_{4-n}[Co(CO)_3]_n$ ($n = 1, 2, 3$)[a]

Product	Reactants and conditions	Ref.
$As_3Co(CO)_3$	$Co_2(CO)_8 + [AsCH_3]_5$, hexane, 200°C, 100 atm CO	7
$As_2Co_2(CO)_6$	$Co_2(CO)_8$ + excess $AsCl_3$, THF	399
$P_2Co_2(CO)_6$	$NaCo(CO)_4 + PX_3$ ($X = Cl, Br$), THF	400
$SPCo_3(CO)_9$	$NaCo(CO)_4 + SPX_3$ ($X = Cl, Br$), THF	400
$Sb_4Co_4(CO)_{12}$	$Co(OAc)_2 \cdot 4H_2O + SbCl_3$, CH_3OH, 150°, high pressure (H_2, CO)	402
$PhCCo_3(CO)_9$	$NaCo(CO)_4 + PhCCl_3$, THF	43
$ClCCo_3(CO)_9$	$Co_2(CO)_8 + CCl_4$, EtOH	404
$PhGeCo_3(CO)_9$	$PhGeCo_3(CO)_{11}$ refluxed in hexane	44
$H_2C_2Co_2(CO)_6$	$Co_2(CO)_8 + HC{\equiv}CH$, petr. ether	405

[a] Many related methods for the preparation of other methinyltricobalt enneacarbonyl species are given in a recent review [401].

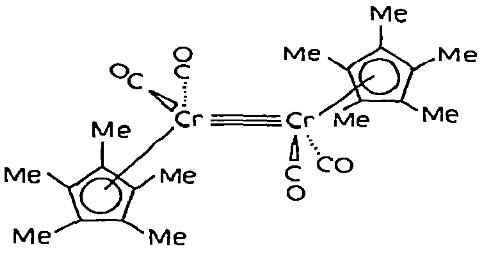
General routes to syntheses of these tetrameric species have not been discovered. The variety of reagents and conditions that have been utilized in the preparation of some of the above compounds may be appreciated from the data in Table 5. In most cases yields of products are low ($< 10\%$).

Monomeric species containing an $M(CO)_3$ unit such as $H_3M(CO)_3$ (M = Co, Rh, Ir) would also have the preferred closed-shell configuration like their main-group analogues, ammonia, phosphine, arsine, etc. Although the unsubstituted carbonyl hydrides are unknown, the substituted species $H_3M(PR_3)_3$, R = alkyl or aryl, M = Co [406] and Ir [407], and $H_3IrCO(PPh_3)_2$ [408], have been reported. Related dihalo derivatives HX_2ML_3 (X = Cl, Br, M = Co, Rh, Ir) are also known. A rather complete listing of these and related substances are given in a recent review on hydride complexes [409].

B. Derivatives of other trianions

Tetrahedral clusters which contain other pseudopnicogen units include $[C_5H_5M(CO)]_4$ (M = Fe [410] and Ru [411]), $[HM(CO)_3]_4$ (M = Ru [412] and Os [413]). An ethylidyne derivative of $[HM(CO)_3]_4$ has been reported, $H_3Ru_3(CO)_9CMe$ [414], that is electronically equivalent to $MeCCo_3(CO)_9$ [401]. A similar compound not containing carbonyls is $MeCNi_3(C_5H_5)_3$ [415], where the π-C_5H_5Ni unit is a 15-electron group. This class of complexes is particularly interesting since they represent one way in which a carbyne may be stabilized by coordination to transition metals. Surprisingly, no similar phosphorus analogues, e.g., P_3CCH_3, have been reported, although they should be capable of existence.

Another way in which phosphorus could stabilize a carbyne would be by forming a P—C triple bond e.g., $P{\equiv}C{-}CH_3$. Such phosphorus analogues of organic nitriles are unknown. However, recently, as was noted in section III, carbynes coordinated to Group VI transition metals in this fashion have been reported; e.g., $Br(CO)_4M{\equiv}C{-}CH_3$, M = Cr, Mo, W [381]. In this case the transition metal pseudopnicogen unit ($X(CO)_4M$, where X is a halogen) is behaving more like nitrogen than the higher homologues. The chemical signigicance of this analogy, however, is presently unknown. For several years nitrogen analogues of carbyne complexes have been known in coordination chemistry. Although many of these species containing a M≡N bond such as OsO_3N^- and $OsNCl_5^{2-}$ are purely inorganic species, there do exist phosphine derivatives of $Cl_2(CO)_3Re{\equiv}N$, such as $Cl_2(PEt_2Ph)_3Re{\equiv}N$, where $Cl_2(CO)_3Re$ is a 15 electron system similar to the $X(CO)_4M$ species of Cr, Mo and W. There seems no reason why similar carbyne complexes containing 15 electron Group VIII organometallic species cannot be made. References to these and other so-called nitrido complexes may be found in a recent review article [419]. Other pseudopnicogen units of the Group VI transition metals, π-$Me_5C_5M(CO)_2$, M = Cr, Mo) [416], are presently unique in their ability to attain closed-shell configurations by dimerizing and forming a formal M—M triple bond. An X-ray crystal structure of the chromium analogue has confirmed the presence of a very short Cr≡Cr bond (2.276Å) [417]. A representation of the structure (XXIII) is shown. The reasons why these 15 electron units form dimers instead of tetramers, as in the case of C_5H_5FeCO or $Co(CO)_3$, are unknown but it may have to do with metal size, steric effects, and other factors. Treatment of $[\pi\text{-}Me_5C_5Cr(CO)_2]_2$ and its molybdenum analogue with a variety of reagents failed to provide evidence that there is any analogy between the chemistry of the M≡M triple bond in these species and the chemistry of the triple bond in main-group species. A summary of these reactions are given below. An indication of the stability of these M≡M triple bonds is provided by its inability to add gaseous HCl in cyclohexane at room temperature [418].



(XXIII)

$$
[Me_5C_5M(CO)_2]_2 \left\{
\begin{array}{l}
\xrightarrow{Na,\,Hg,\,THF} Me_5C_5M(CO)_3^- \xrightarrow{Ph_3SnCl} Ph_3SnM(CO)_3C_5Me_5 \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (19\%\ Cr,\ 5\%\ Mo) \\
\xrightarrow{I_2} Me_5C_5M(CO)_3I\ (8\%\ Cr,\ 26\%\ Mo) \\
\xrightarrow{NO} Me_5C_5M(CO)_2NO\ (12\%\ Cr,\ 37\%\ Mo)
\end{array}
\right.
$$

(Data from reference 418)

V. Addendum

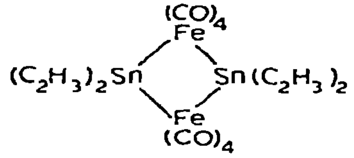
Since the completion of the original manuscript which covers the literature through to July 1974, several other relevant articles on metal carbonyl anion chemistry have been included.

A. Carbonyl dianions

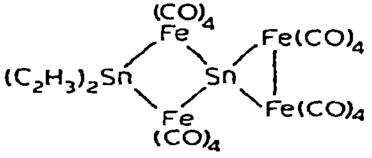
The reactions of $Na_2Fe(CO)_4$ with $(\text{vinyl})_2Sn(O_2CCF_3)_2$ [428] and $(CH_3)_2C(NO)Br$ [429] have been investigated and proceed according to the following equations:

$$Na_2Fe(CO)_4 + (\text{vinyl})_2Sn(O_2CCF_3)_2 \rightarrow \begin{array}{l}(\text{vinyl})_2Sn_2Fe_2(CO)_8\\ (\text{major product} = A)\\ \\ + (\text{vinyl})_2Sn_2Fe_4(CO)_{16}\\ (\text{minor product} = B)\end{array}$$

Structures of A and B postulated on the basis of infrared, mass spectroscopy and analytical data are the following:



(A)



(B)

$$Na_2Fe(CO)_4 + (CH_3)_2C(NO)Br \rightarrow [(H_3C)_2C{=}NFe(CO)_3]_2 \qquad [429]$$

Included in ref. 429 are the results of the reaction of $Na_2M_2(CO)_{10}$ (M = Cr, W) with the same nitrosyl halide:

$$\begin{array}{ll}Na_2M_2(CO)_{10} + (CH_3)_2C(NO)Br \rightarrow (CH_3)_2C{=}NHM(CO)_5 & [429]\\ \quad (M = Cr, W) \qquad\qquad\qquad\qquad (3\text{-}5\%\ \text{yield}) & \end{array}$$

The following monomeric substituted carbonyl dianions should be included in the original list: $Re(CO)_3(NCS)_3^{2-}$ [430], $Re(CO)_3I_3^{2-}$ [431], $Ir(CO)X_5^{2-}$ (X = Cl, Br, I) [432] and $Ni(CO)_2(GeCl_3)_2^{2-}$ [433]. Other similar species may also exist.

B. Carbonyl trianions

A number of cyanide substituted carbonyl trianions are known, including $K_3Fe(CO)(CN)_5$ [434] and $K_3M(CO)_3(CN)_3$ (M = Mo, W) [312]. Also, recently a paper described the preparation of the novel species $[(C_2H_5)_4N]_3[Mo(CO)_3(GeCl_3)_3]$ from the reaction of $(C_2H_5)_4N[GeCl_3]$ with $(\text{mesitylene})Mo(CO)_3$ [433].

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