Some Applications of Metal Carbonyl Anions in the Synthesis of Unusual Organometallic Compounds

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Metal carbonyls have been known for over 75 years. Within the last 40 years numerous anionic derivatives of metal carbonyls have been synthesized. More recently some of these metal carbonyl anions have been used as intermediates of the synthesis of unusual organometallic compounds. This Account summarizes some of the recent results in this area, with particular emphasis on results from my own laboratory.

The preparations, properties, and reactions of metal carbonyl anions have been the subjects of comprehensive reviews[1,2] to which the reader is referred for more detailed information than that presented in this Account.

Preparation of Metal Carbonyl Anions

Metal carbonyl anions used for preparative purposes are most often used as solutions of their sodium salts in tetrahydrofuran. These are generally prepared by reduction of binuclear (and sometimes trinuclear) metal carbonyl derivatives in tetrahydrofuran solution with a dilute sodium amalgam at room temperature. Equations 1–3 are illustrative. All of the metal carbonyl starting materials required for these preparations are either commercially available or readily prepared by well-established procedures.

$$\mathrm{Co_2(CO)_8 + 2Na \longrightarrow 2NaCo(CO)_4} \qquad (1)^{3}$$

$$\mathrm{M_2(CO)_{10} + 2Na \longrightarrow 2NaM(CO)_5\ (M = Mn\ or\ Re)} \qquad (2)^{4}$$

$$\mathrm{Fe_3(CO)_{12} + 6Na \longrightarrow 3Na_2Fe(CO)_4} \qquad (3)^{5}$$

Similar techniques are useful for the preparation of sodium and potassium salts of substituted metal carbonyl anions. For example, procedures 4–6 may be used for preparation of alkali metal salts of cyclopentadienylmetal carbonyl anions. Sodium salts of the type $NaM(CO)_3C_5H_5$ (II, M = Cr, Mo, or W) can also be prepared by reaction of the corresponding metal hexacarbonyl with sodium cyclopentadienide in an ethereal solvent at elevated temperatures, a reaction in which three carbonyl groups are displaced.[10] This reaction is analogous to the displacement of three carbonyl groups from the metal hexacarbonyls with various neutral aromatic hydrocarbons such as benzene.[11] The preparation of $NaMo(CO)_3C_5H_5$ from $Mo(CO)_6$ and NaC_5H_5 has the advantage over its preparation from $[C_5H_5Mo(CO)_3]_2$ and sodium amalgam in that $Mo(CO)_6$ is more readily available and less expensive than $[C_5H_5Mo(CO)_3]_2$.

$$\mathrm{[C_5H_5NiCO]_2 + 2K \longrightarrow 2KNiCOC_5H_5} \qquad (4)^{6}$$

$$\mathrm{[C_5H_5M(CO)_2]_2 + 2Na \longrightarrow \underset{I,\ M\ =\ Fe^{7}\ or\ Ru^{8}}{2NaM(CO)_2C_5H_5}} \qquad (5)$$

$$\mathrm{[C_5H_5Mo(CO)_3]_2 + 2Na \longrightarrow \underset{II,\ M\ =\ Mo}{2NaMo(CO)_3C_5H_5}} \qquad (6)^{9}$$

$$\mathrm{M(CO)_6 + NaC_5H_5 \longrightarrow NaM(CO)_3C_5H_5 + 3CO}$$
$$\mathrm{M = Cr,\ Mo,\ and\ W}$$

Metal carbonyl anions with substituents other than cyclopentadienyl are also known. An indenylmetal carbonyl anion can be prepared as its sodium salt by the method[12]

$$\mathrm{[C_9H_7Mo(CO)_3]_2 + 2Na \longrightarrow \underset{III}{2Na[Mo(CO)_3C_9H_7]}}$$

Equations 7 and 8 exemplify preparations of synthetically useful metal carbonyl anions with organophosphorus substituents. Such substituted metal carbonyl anions cannot be prepared by heating an unsubstituted metal carbonyl anion with the free ligand since in most cases the carbonyl groups in anionic derivatives are too strongly bonded to the metal atom to be so displaced. This strong bonding from the metal atom to the carbonyl groups in anionic metal carbonyl derivatives is a consequence of the relatively high negative charge on the metal atom which results in unusually strong $d\pi$–$p\pi^*$ partial double bonding involving back-donation of metal electrons to antibonding orbitals

$$\mathrm{[R_3PMn(CO)_4]_2 + 2Na \longrightarrow 2Na[Mn(CO)_4PR_3]} \qquad (7)$$
$$\mathrm{R = C_6H_5,^{13}\ OC_6H_5,^{14}\ N(CH_3)_2,^{15}\ etc.}$$

$$\mathrm{[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2 + 2Na \longrightarrow 2Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]} \qquad (8)^{16}$$

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(1) W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, **72**, 795 (1960).

(2) R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964).

(3) W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch. B*, **13**, 192 (1958).

(4) W. Hieber and G. Wagner, *ibid.*, **12**, 178 (1957); **13**, 339 (1958).

(5) R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 3604 (1961).

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(9) E. W. Abel, A. Singh, and G. Wilkinson, *ibid.*, 1321 (1960); R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

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(11) E. O., Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *Z. Naturforsch. B*, **13**, 458 (1958); *Ber.*, **92**, 2763 (1958); B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959); G. Natta, R. Ercoli, F. Calderazzo, and S. Santambrogio, *Chim. Ind.* (*Milan*), **40**, 1003 (1958).

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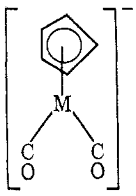
of the carbonyl groups. Spectroscopic evidence for this effect is given by the relatively low infrared ν(CO) frequencies in metal carbonyl anions. These frequencies are indicative of a relatively low carbon–oxygen bond order as would arise from relatively large back-donation into the antibonding orbitals of the carbonyl groups.



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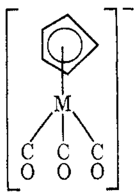

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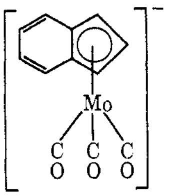

III

Most of these preparations of sodium salts of metal carbonyl anions utilize a dilute sodium amalgam as the reducing agent. A disadvantage of this method is the tendency for the large amounts of mercury in the system to form nonionic mercury derivatives of the metal carbonyls as by-products.[17] These mercury derivatives can complicate the isolation of products from the further reactions of metal carbonyl anions. For this reason and because of the relatively high cost and toxicity of the large amounts of mercury required, there is incentive to develop simple and reliable alternative procedures for generating metal carbonyl anions. McClellan[18] has reported the successful use of lithium wire in place of sodium amalgam for the reduction of binuclear metal carbonyls (*e.g.*, $Mn_2(CO)_{10}$ and $Co_2(CO)_8$) to the corresponding metal carbonyl anions, but the author has not found this procedure to be particularly reliable, probably owing to differences in the type of mechanical stirring and in the quality of the lithium wire. A more promising, but as yet largely untested, procedure for generating reactive magnesium derivatives, reported by Burlitch and Ulmer,[19] utilizes the reactions of metal carbonyl halides with magnesium turnings in tetrahydrofuran, analogous to the preparation of Grignard reagents. Thus

$$Mn(CO)_5Br + Mg \longrightarrow \text{“}BrMgMn(CO)_5\text{”}$$
$$C_5H_5Fe(CO)_2Cl + Mg \longrightarrow \text{“}ClMgFe(CO)_2C_5H_5\text{”}$$

Modifications of this Burlitch–Ulmer procedure can be used to generate the magnesium derivatives from binuclear metal carbonyl derivatives which are more readily available than the corresponding metal carbonyl halides. Thus

$$Mn_2(CO)_{10} + 1,2\text{-}C_2H_4Br_2 + 2Mg \longrightarrow 2\text{“}BrMgMn(CO)_5\text{”} + CH_2{=}CH_2$$
$$[C_5H_5Fe(CO)_2]_2 + 1,2\text{-}C_2H_4Br_2 + 2Mg \longrightarrow 2\text{“}BrMgFe(CO)_2C_5H_5\text{”} + CH_2{=}CH_2$$

Preliminary indications[19] suggest that these magnesium derivatives of metal carbonyl anions have preparative utility similar to that of the corresponding sodium salts discussed in this Account.

Reactions of Metal Carbonyl Anions

The preparative applications of metal carbonyl anions depend on their reactivity as nucleophiles toward electrophilic reagents. Of particular importance is the nucleophilic displacement by metal carbonyl anions of halide from a variety of halides, both organic and inorganic, according to the general scheme for metal carbonyl anions and cyclopentadienylmetal carbonyl anions

$$[(C_5H_5)_mM(CO)_n]^- + RX \longrightarrow RM(CO)_n(C_5H_5)_m + X^-$$
$$m = 0 \text{ or } 1;\ n = 1\text{–}5 \text{ depending on M}$$

This process results in the formation of a new chemical bond between some atom of the R group and the central metal atom, thereby increasing the coordination number of the central metal atom by one. This synthetic procedure is therefore useful for the preparation of numerous unusual compounds with transition metals bonded to other elements of the periodic table, including carbon, silicon, germanium, tin, lead, boron,[20] gallium,[21] thallium,[21] and other transition metals. Many of the types of chemical bonds which can be formed by using metal carbonyl anions cannot be formed efficiently by other synthetic methods. For this reason many organometallic compounds prepared from metal carbonyl anions are of fundamental importance in studies of chemical bonding. Also work of this type is of ultimate practical significance in areas such as catalysis.

The nucleophilicities of anionic metal carbonyl derivatives vary enormously. For this reason, there are major differences between the chemistries of different metal carbonyl anions. In order to evaluate their nucleophilicities, the relative rates of reactions of various metal carbonyl anions with organic halides (methyl iodide, ethyl bromide, and isopropyl bromide) were measured using metal carbonyl anions generated on a microscale by electrochemical reduction of the corresponding binuclear derivative.[22] The relative nucleophilicities listed in Table I were thus determined.

Inspection of Table I suggests that the following factors affect the nucleophilicity of metal carbonyl anions.

(1) Coordination Number of the Central Metal Atom. A nucleophilic displacement reaction of a metal carbonyl anion forms a new bond to the central metal atom and hence increases its coordination number by one. In the cases of transition metals which form stable carbonyl derivatives, a coordination number of six is generally more favorable than a coordination number of five or seven in the absence of changes in electronic configuration[23] which likewise affect markedly the stabilities of metal carbonyl derivatives. For this reason the $Co(CO)_4^-$ anion, in which the coordination

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(17) R. B. King, *J. Inorg. Nucl. Chem.*, **25**, 1296 (1963).

(18) W. R. McClellan, *J. Amer. Chem. Soc.*, **83**, 1598 (1961).

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Table I

Relative Nucleophilicities of Some Metal Carbonyl Anions[a]

Anion	Relative nucleophilicity[b]
$C_5H_5Fe(CO)_2^-$	70,000,000
$C_5H_5Ru(CO)_2^-$	7,500,000
$C_5H_5NiCO^-$	5,500,000
$Re(CO)_5^-$	25,000
$C_5H_5W(CO)_3^-$	~500
$Mn(CO)_5^-$	77
$C_5H_5Mo(CO)_3^-$	67
$C_5H_5Cr(CO)_3^-$	4
$Co(CO)_4^-$	1

[a] Data reported by R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, **88,** 5121 (1966). [b] These relative nucleophilicities were measured electrochemically in 1,2-dimethoxyethane solution in the presence of tetrabutylammonium perchlorate. The nucleophilicity of $Co(CO)_4^-$ is arbitrarily taken as 1.

number of the central cobalt atom changes from four to five during a nucleophilic displacement reaction, is less nucleophilic than the $Mn(CO)_5^-$ anion in which the coordination number of the central manganese atom changes from five to six.

(2) **Size of the Central Metal Atom.** In the series $M(CO)_5^-$(M = Mn or Re) and $C_5H_5M(CO)_3^-$ (M = Cr, Mo, or W) the nucleophilicity increases as the central metal atom becomes heavier. However, the decrease in nucleophilicity in going from $C_5H_5Fe(CO)_2^-$ to its ruthenium analog counters this trend for reasons that are not clearly understood.

(3) **π-Acceptor Strength of the Ligands Attached to the Central Metal Atom.** The carbonyl group is a stronger π acceptor than almost any other ligand which bonds to transition metals (except for possibly trifluorophosphine and the nitrosyl group). For this reason replacement of carbonyl groups with other ligands such as cyclopentadienyl and triphenylphosphine almost invariably increases the negative charge on the central metal atom and hence its nucleophilicity. This accounts for the increases in nucleophilicity upon replacing three carbonyl groups with a π-cyclopentadienyl ring such as in going from $Mn(CO)_5^-$ to $C_5H_5Fe(CO)_2^-$ or from $Co(CO)_4^-$ to $C_5H_5NiCO^-$.

The carbonyl groups in metal carbonyl anions are relatively strongly bonded to the central metal atom because of the relatively strong $d\pi$–$p\pi^*$ partial double bonding between the central metal atom and the carbonyl groups. However, much of this negative charge is removed when a metal carbonyl anion, $[(C_5H_5)_mM(CO)_n]^-$, is converted to the corresponding neutral $RM(CO)_n(C_5H_5)_m$ derivative. For this reason some $RM(CO)_n(C_5H_5)_m$ derivatives undergo facile loss of carbon monoxide.

Such decarbonylation reactions can take place in cases where the R group, which is a one-electron donor in the originally formed $RM(CO)_n(C_5H_5)_m$ compound, can be modified in such a way as to donate three or more electrons to the central metal atom. In essentially all of the complexes discussed in this Account the central metal atom has the 18-electron configuration of the next rare gas.[23] Maintenance of the 18-electron rare gas configuration means that the loss of each carbonyl group in the decarbonylation reaction must result in an increase by two of the number of electrons donated to the central metal atom by some other ligand.

The decarbonylation of acyl transition metal derivatives is a particularly important reaction and may be represented by

$$RCOM(CO)_n(C_5H_5)_m \longrightarrow RM(CO)_n(C_5H_5)_m + CO$$

This type of reaction was first reported for manganese carbonyl derivatives.[24] Thus acetyl chloride reacts with the sodium salt $NaMn(CO)_5$ to form the white air-stable crystalline acetyl derivative $CH_3COMn(CO)_5$ according to the following equation, which is an example of a nucleophilic displacement reaction involving a metal carbonyl anion.

$$NaMn(CO)_5 + CH_3COCl \longrightarrow CH_3COMn(CO)_5 + NaCl$$

The acyl carbonyl group in $CH_3COMn(CO)_5$ and related compounds exhibits a characteristic infrared ν(CO) frequency around 1600 cm^{-1} which differs appreciably from the characteristic frequencies of terminal metal carbonyl groups. Mild heating of $CH_3COMn(CO)_5$ results in evolution of carbon monoxide and formation of the corresponding methyl derivative with concurrent disappearance of the infrared acyl carbonyl frequency around 1600 cm^{-1} according to

$$CH_3COMn(CO)_5 \longrightarrow CH_3Mn(CO)_5 + CO$$

The $CH_3Mn(CO)_5$ prepared by the decarbonylation of $CH_3COMn(CO)_5$ is an air-stable white crystalline solid identical with the compound prepared by reaction of $NaMn(CO)_5$ with methyl iodide. In this case the decarbonylation reaction is reversible since $CH_3Mn(CO)_5$ reacts with carbon monoxide at 25° and 35 atm to form the acetyl derivative $CH_3COMn(CO)_5$. However, in cases of $RMn(CO)_5$ derivatives where the R group is relatively electronegative (*e.g.*, $CF_3Mn(CO)_5$), the manganese–R bond is so strong that carbon monoxide cannot be inserted into this bond to form the corresponding acyl derivative $RCOMn(CO)_5$.[25]

Isotopic labeling has demonstrated that the CO group which is lost comes from a terminal metal carbonyl group rather than from the acyl carbonyl group, *i.e.*[26]

$$RC^*OMn(CO)_5 \longrightarrow RMn(CO)_4C^*O + CO$$

During the course of the decarbonylation of acyl derivatives the one-electron donor RCO group is converted to two groups: a one-electron donor R group and a two-electron donor CO group. In this manner the extra two electrons for the central metal atom are obtained to make up for the loss of two electrons upon loss of the terminal carbonyl group, thereby permitting the central

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(24) R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22,** 598 (1957); T. H. Coffield, J. Kozikowski and R. D. Closson, *ibid.*, **22,** 598 (1957).

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(26) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10,** 101 (1967).

metal atom to retain the favored 18-electron rare gas configuration.[23]

Qualitative observations indicate that there are major differences in the relative ease of decarbonylation of different acyl derivatives $RCOM(CO)_n(C_5H_5)_m$, although no quantitative measurements have been made comparable to the quantitative studies on the nucleophilicities of various metal carbonyl anions.[22] Such observations suggest the following approximate order of relative ease of decarbonylation for various $RCOM(CO)_n(C_5H_5)_m$ derivatives: $RCOCo(CO)_4$ (most easily decarbonylated) > $(RCO)_2Fe(CO)_4$ > $RCOMn(CO)_5$ > $RCORe(CO)_5 \sim RCOMo(CO)_3C_5H_5 > RCOFe(CO)_2C_5H_5 > RCOW(CO)_3C_5H_5$.

The following reported decarbonylation conditions for the decarbonylation of heptafluorobutyryl (C_3F_7CO) derivatives both illustrate empirical evidence for the above relative ease of decarbonylation sequence and exemplify conditions for the decarbonylation of various types of acyl transition metal derivatives: (a) $C_3F_7COCo(CO)_4$ to $C_3F_7Co(CO)_4$: this decarbonylation occurs spontaneously upon allowing $LiCo(CO)_4$ to react with C_3F_7COCl at room temperature;[18] (b) $(C_3F_7CO)_2Fe(CO)_4$ to $(C_3F_7)_2Fe(CO)_4$: this decarbonylation occurs spontaneously upon allowing $Na_2Fe(CO)_4$ to react with C_3F_7COCl in boiling tetrahydrofuran (~65°);[5,27] (c) $C_3F_7COMn(CO)_5$ to $C_3F_7Mn(CO)_5$: this decarbonylation occurs upon heating pure $C_3F_7COMn(CO)_5$ under vacuum to about 80° for several hours;[28] (d) $C_3F_7CORe(CO)_5$ to $C_3F_7Re(CO)_5$: this decarbonylation occurs upon heating pure $C_3F_7CORe(CO)_5$ under vacuum to about 120° for several hours;[28] (e) $C_3F_7COMo(CO)_3C_5H_5$ to $C_3F_7Mo(CO)_3C_5H_5$: this decarbonylation occurs upon heating pure $C_3F_7COMo(CO)_3C_5H_5$ to 120° for several hours;[29] (f) $C_3F_7COFe(CO)_2C_5H_5$ to $C_3F_7Fe(CO)_2C_5H_5$: this decarbonylation occurs upon ultraviolet irradiation of $C_3F_7COFe(CO)_2C_5H_5$ in hexane solution; however, similar decarbonylations of $RCOFe(CO)_2C_5H_5$ could not be effected by purely thermal procedures such as are effective for the decarbonylation of $RCOMo(CO)_3C_5H_5$ derivatives;[29] (g) $C_3F_7COW(CO)_3C_5H_5$ to $C_3F_7W(CO)_3C_5H_5$: this decarbonylation did not take place either under conditions where $C_3F_7COFe(CO)_2C_5H_5$ could be converted to $C_3F_7Fe(CO)_2C_5H_5$ or under conditions where $C_3F_7COMo(CO)_3C_5H_5$ could be converted to $C_3F_7Mo(CO)_3C_5H_5$.[29]

Reversible decarbonylations of relatively labile $RCOCo(CO)_4$ compounds are undoubtedly involved in the oxo process, hydroformylation reactions, and other commercially important cobalt-catalyzed reactions of carbon monoxide under pressure with various unsaturated organic compounds.[30]

There is no correlation between the nucleophilicity of a metal carbonyl anion and the ease of decarbonylation of the corresponding $RCOM(CO)_n(C_5H_5)_m$ derivative. The $Co(CO)_4^-$ anion has a low nucleophilicity and the corresponding $RCOCo(CO)_4$ derivatives are readily decarbonylated. The $C_5H_5W(CO)_3^-$ anion has a medium low nucleophilicity and the $C_5H_5Fe(CO)_2^-$ anion an extremely high nucleophilicity, but the corresponding $RCOW(CO)_3C_5H_5$ and $RCOFe(CO)_2C_5H_5$ derivatives both are decarbonylated with great difficulty. The two considerations of nucleophilicity and ease of decarbonylation are of great importance in selecting metal carbonyl anions for various preparative applications.

Alkylation of Metal Carbonyl Anions

All of the metal carbonyl anions listed in Table I react with methyl iodide to form methyl derivatives, with the methyl group directly bonded to the transition metal. These methyl derivatives represent a wide range of stabilities from $CH_3Co(CO)_4$[3] which decomposes above −35° to $CH_3W(CO)_3C_5H_5$ which is stable above +145° and indefinitely stable upon exposure to air.[31] These methyl derivatives of transition metals undergo a wide variety of insertion reactions, as exemplified by reactions 9–12 of $CH_3Fe(CO)_2C_5H_5$.

$$CH_3Fe(CO)_2C_5H_5 + CO \longrightarrow CH_3COFe(CO)_2C_5H_5 \quad (9)$$

$$CH_3Fe(CO)_2C_5H_5 + SO_2 \longrightarrow \underset{\text{IV}}{CH_3SO_2Fe(CO)_2C_5H_5} \quad (10)^{32}$$

$$CH_3Fe(CO)_2C_5H_5 + (C_6H_5)_3P \longrightarrow \underset{\text{V}}{CH_3COFe(CO)[P(C_6H_5)_3](C_5H_5)} \quad (11)^{33}$$

$$CH_3Fe(CO)_2C_5H_5 + CF_3CN \longrightarrow \underset{\text{VI}}{CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)} + ? \quad (12)^{34}$$

The reaction with triphenylphosphine to form an acyliron derivative is closely related to the insertion of carbon monoxide to form an acyl derivative in that the incoming ligand displaces a carbonyl group from the metal atom which is the species that then actually inserts into the alkyl–iron bond. This contrasts with the reaction of $CH_3Fe(CO)_2C_5H_5$ with sulfur dioxide where the incoming ligand inserts directly into the alkyl–iron bond, thereby providing one of the best synthetic routes to *S*-alkylsulfinato complexes. The reaction of $CH_3Fe(CO)_2C_5H_5$ with trifluoroacetonitrile provided the first route to an imino–transition metal complex (VI) analogous to an acyl–transition metal complex, but with an NH group in place of the oxygen atom.

Metal carbonyl anions react with other reactive alkyl halides to form the corresponding alkyl–transition metal derivatives. However, the products formed from metal

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

(28) H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch. B*, **15**, 763 (1960).

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(32) J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **88**, 4862 (1966).

(33) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).

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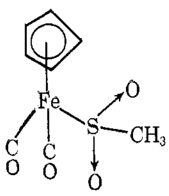

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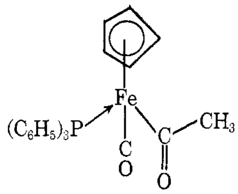

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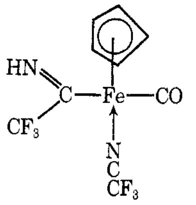
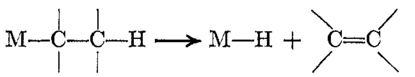


VI

carbonyl anions and organic halides with hydrogen atoms attached to an sp^3 carbon atom in the β position relative to the halogen atom become progressively less stable as the number of such hydrogen atoms increases. Thus the stability of alkyliron derivatives of the type $RFe(CO)_2C_5H_5$ decreases in the sequence:[35] R = methyl (most stable) > ethyl > isopropyl > *tert*-butyl (least stable). This instability appears to arise from the tendency of alkyl transition metal derivatives to decompose into olefins according to the sequence



$$M{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H \longrightarrow M{-}H + {>}C{=}C{<}$$

The resulting hydride $HFe(CO)_2C_5H_5$ decomposes readily into $[C_5H_5Fe(CO)_2]_2$ at room temperature, particularly upon exposure to air. In the case of the *tert*-butyl derivatives the tendency for olefin elimination is sufficiently great that the reaction between certain metal carbonyl anions and *tert*-butyl chloride can be used for the preparation of the corresponding hydride, *e.g.*[35]

$$NaFe(CO)_2C_5H_5 + (CH_3)_3CCl \longrightarrow HFe(CO)_2C_5H_5 + (CH_3)_2C{=}CH_2 + NaCl$$

This reaction appears to be the best known way to prepare $HFe(CO)_2C_5H_5$. Related reactions are useful for generating relatively unstable metal carbonyl hydrides in the absence of acids.

Some organic halides do not react efficiently with metal carbonyl anions. Thus iodobenzene reacts with the extremely nucleophilic $NaFe(CO)_2C_5H_5$ to give only a 2% yield of the corresponding phenyl derivative $C_6H_5Fe(CO)_2C_5H_5$ and is apparently unreactive toward less reactive metal carbonyl anions such as $NaMo(CO)_3C_5H_5$.[31] Vinyl chloride is similarly unreactive toward metal carbonyl anions.[36] For this reason phenyl and vinyl derivatives of transition metals are often best prepared by the following two-step sequence: (a) reaction of the metal carbonyl anion with the corresponding *acyl* chloride (*i.e.*, benzoyl or acryloyl chloride); (b) decarbonylation of the resulting acyl derivative. Equations 13 and 14 illustrate applications of this two-step procedure for the preparation of phenyl and vinyl derivatives. The

$$NaMn(CO)_5 + C_6H_5COCl \xrightarrow{THF} C_6H_5COMn(CO)_5 + NaCl$$

$$C_6H_5COMn(CO)_5 \xrightarrow{\Delta} C_6H_5Mn(CO)_5 + CO \qquad (13)^{24}$$

vinyliron compound VII is apparently the only known

$$NaFe(CO)_2C_5H_5 + CH_2{=}CHCOCl \xrightarrow{THF} CH_2{=}CHCOFe(CO)_2C_5H_5 + NaCl$$

$$CH_2{=}CHCOFe(CO)_2C_5H_5 \xrightarrow{uv} \underset{\text{VII}}{CH_2{=}CHFe(CO)_2C_5H_5} \qquad (14)^{29}$$

example of a metal carbonyl derivative of an unsubstituted uncomplexed vinyl group.

The unreactivity of most aryl halides toward metal carbonyl anions has led to the use of more powerful arylating agents.

Thus diphenyliodonium iodide reacts with $NaFe(CO)_2C_5H_5$ in tetrahydrofuran solution to give an 18% yield of $C_6H_5Fe(CO)_2C_5H_5$ according to eq 15.[37] Aryl-

$$NaFe(CO)_2C_5H_5 + [(C_6H_5)_2I]I \xrightarrow{THF} C_6H_5Fe(CO)_2C_5H_5 + NaI + C_6H_5I \qquad (15)$$

diazonium salts also react with $NaFe(CO)_2C_5H_5$ with evolution of nitrogen to form aryliron derivatives in low yield according to eq 16.[38] This contrasts with the

$$NaFe(CO)_2C_5H_5 + C_6H_5N_2^+BF_4^- \xrightarrow{THF} C_6H_5Fe(CO)_2C_5H_5 + NaBF_4 + N_2 \qquad (16)$$

reactions of aryldiazonium salts with the sodium salt $NaMo(CO)_3C_5H_5$ which result in the evolution of carbon monoxide to form arylazo derivatives, *e.g.*,[39] eq 17.

$$NaMo(CO)_3C_5H_5 + C_6H_5N_2^+BF_4^- \xrightarrow{THF} \underset{\text{VIII}}{C_6H_5N_2Mo(CO)_2C_5H_5} + NaBF_4 + CO \qquad (17)$$

The arylazo group in VIII and related compounds acts as a neutral three-electron donor[23] like the more familiar nitrosyl group in metal nitrosyls. The differing behavior of aryldiazonium salts upon reaction with $NaFe(CO)_2C_5H_5$ and $NaMo(CO)_3C_5H_5$ is apparently related to the greater ease of decarbonylation of $RMo(CO)_3C_5H_5$ derivatives relative to corresponding $RFe(CO)_2C_5H_5$ derivatives as discussed above.

Some unusual compounds are obtained from reactions of metal carbonyl anions with α,ω-dibromoalkanes of the type $Br(CH_2)_nBr$. The very nucleophilic $NaFe(CO)_2C_5H_5$ replaces both halogen atoms in the α,ω-dibromoalkanes $Br(CH_2)_nBr$ (n = 3, 4, 5, and 6) to form diiron derivatives of the type $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ (IX, n = 3, 4, 5, and 6).[40] However, the less nucleophilic sodium salts $NaM(CO)_3C_5H_5$ (M = Mo and W) replace only one halogen atom in the α,ω-dibromoalkanes $Br(CH_2)_nBr$ (n = 3 and 4) to form the bromoalkyl derivatives $Br(CH_2)_nM(CO)_3C_5H_5$ (X, M = Mo and W; n = 3 and 4).[41] Attempts to replace the remaining bromine atom in the molybdenum deriva-

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(35) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

(36) M. L. H. Green, M. Ishaq, and T. Mole, *Z. Naturforsch. B*, **20**, 598 (1965).

(37) A. N. Nesmeyanov, Yu. A. Chapovskii, B. V. Lokshia, I. V. Polovyanyuk, and L. G. Makarova, *Dokl. Akad. Nauk SSSR*, **166**, 1125 (1966).

(38) A. N. Nesmeyanov, Yu. A. Chapovskii, I. V. Polovyanyuk, and L. G. Makarova, *J. Organometal. Chem.*, **7**, 329 (1967).

(39) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).

(40) R. B. King, *ibid.*, **2**, 531 (1963).

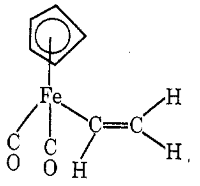
(41) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **7**, 311 (1967).

tives $\mathrm{Br(CH_2)_nMo(CO)_3C_5H_5}$ (X, M = Mo; n = 3 and 4) with an iron atom to give "mixed" iron–molybdenum polymethylene derivatives using the very nucleophilic $\mathrm{NaFe(CO)_2C_5H_5}$ result instead in reaction 18.[41] This unusual "transmetalation" reaction

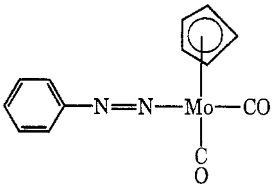
$$\mathrm{Br(CH_2)_nMo(CO)_3C_5H_5 + 2NaFe(CO)_2C_5H_5 \longrightarrow (CH_2)_n[Fe(CO)_2C_5H_5]_2 + NaBr + NaMo(CO)_3C_5H_5} \quad (18)$$

may be considered as the displacement of the anion $\mathrm{C_5H_5Mo(CO)_3^-}$ by the much more nucleophilic anion $\mathrm{C_5H_5Fe(CO)_2^-}$.

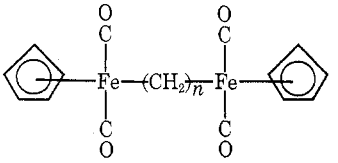
The iron compounds $\mathrm{(CH_2)_n[Fe(CO)_2C_5H_5]_2}$ (IX, n = 3, 4, 5, and 6) are yellow-orange crystalline solids similar in color to the corresponding methyl derivative $\mathrm{CH_3Fe(CO)_2C_5H_5}$.[40] The nmr spectrum of each of the iron compounds $\mathrm{(CH_2)_n[Fe(CO)_2C_5H_5]_2}$ (IX, n = 3, 4, 5, and 6) exhibits a sharp singlet resonance around τ 8.6 corresponding to all of the $\mathrm{CH_2}$ protons, including even those adjacent to the iron atom. This indicates that the $\mathrm{C_5H_5Fe(CO)_2}$ group fortuitously has the same effect on nmr chemical shifts as a $\mathrm{CH_2}$ group. These properties of the iron compound $\mathrm{(CH_2)_3[Fe(CO)_2C_5H_5]_2}$ (IX, n = 3) are very different from those of the corresponding manganese compound $\mathrm{(CH_2)_3[Mn(CO)_5]_2}$ similarly obtained from 1,3-dibromopropane and $\mathrm{NaMn(CO)_5}$.[42] The manganese compound $\mathrm{(CH_2)_3[Mn(CO)_5]_2}$ is a bright yellow solid, while $\mathrm{CH_3Mn(CO)_5}$ is white. Furthermore, the proton nmr spectrum of $\mathrm{(CH_2)_3[Mn(CO)_5]_2}$ exhibits three resonances in a 1:1:1 relative intensity ratio, indicating the six methylene protons to be three nonequivalent pairs. These properties are clearly inconsistent with formulation as a simple trimethylene chain with $\mathrm{Mn(CO)_5}$ groups at each end analogous to structure IX (n = 3) for the iron compound $\mathrm{(CH_2)_3[Fe(CO)_2C_5H_5]_2}$. Several possible structures, all rather strange ones, have been postulated for this enigmatic $\mathrm{(CH_2)_3[Mn(CO)_5]_2}$, mainly in private conversations and correspondence, but none of these has been conclusively demonstrated by unambiguous techniques such as X-ray crystallography. A rhenium analog could not be prepared by reaction of $\mathrm{NaRe(CO)_5}$ with 1,3-dibromopropane under conditions that were successful for the preparation of $\mathrm{(CH_2)_3[Mn(CO)_5]_2}$.[43]



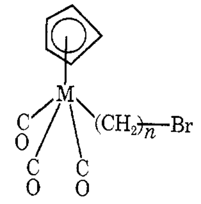
VII



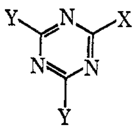
VIII



IX



X



XI

Another polyhalide which has been allowed to react with metal carbonyl anions is cyanuric chloride, $\mathrm{C_3N_3Cl_3}$ (XI, X = Y = Cl).[40,42] Only two of the three chlorine atoms of cyanuric chloride are replaced by transition metals upon reaction with metal carbonyl anions. Thus reactions of cyanuric chloride with $\mathrm{NaFe(CO)_2C_5H_5}$ and $\mathrm{NaMn(CO)_5}$ give orange $\mathrm{C_3N_3Cl[Fe(CO)_2C_5H_5]_2}$ (XI, X = Cl; Y = $\mathrm{Fe(CO)_2C_5H_5}$) and white $\mathrm{C_3N_3Cl[Mn(CO)_5]_2}$ (XI, X = Cl; Y = $\mathrm{Mn(CO)_5}$), respectively.

Fluorocarbon Derivatives of Metal Carbonyls

Metal carbonyl anions are sometimes useful for the preparation of fluorocarbon derivatives of metal carbonyls. However, reactions of metal carbonyl anions with perfluoroalkyl iodides do not yield perfluoroalkyl metal carbonyl derivatives but instead yield metal carbonyl iodides, *e.g.*[44]

$$\mathrm{NaMn(CO)_5 + C_2F_5I \xrightarrow{THF} Mn(CO)_5I + NaF + CF_2{=}CF_2}$$

The difference in the behavior of perfluoroalkyl iodides and that of nonfluorinated alkyl iodides is a consequence of the large cumulative inductive effect of the multiple fluorine atoms which makes the carbon atom of the carbon–iodine bond negative relative to the iodine atom. Sometimes perfluoroalkyl iodides are useful as mild reagents for the conversion of metal carbonyl anions to the corresponding metal carbonyl iodides.

A two-step procedure involving decarbonylation of the corresponding perfluoroacyl intermediate is effective in converting metal carbonyl anions to their perfluoroalkyl derivatives. This procedure is similar to that discussed above for the preparation of vinyl- and phenylmetal carbonyl derivatives and is exemplified by the following preparations of perfluoroalkylmetal carbonyl derivatives (eq 19–21). Incidentally,

$$\mathrm{NaMn(CO)_5 + (CF_3CO)_2O \xrightarrow{THF} CF_3COMn(CO)_5 + CF_3CO_2Na}$$

$$\mathrm{CF_3COMn(CO)_5 \xrightarrow{\Delta} CF_3Mn(CO)_5 + CO} \quad (19)^{18}$$

$$\mathrm{NaFe(CO)_2C_5H_5 + C_2F_5COCl \xrightarrow{THF} C_2F_5COFe(CO)_2C_5H_5 + NaCl}$$

$$\mathrm{C_2F_5COFe(CO)_2C_5H_5 \xrightarrow[hexane]{uv} C_2F_5Fe(CO)_2C_5H_5 + CO} \quad (20)^{29}$$

$$\mathrm{2NaMn(CO)_5 + ClCOCF_2CF_2CF_2COCl \xrightarrow{THF} (CO)_5MnCOCF_2CF_2CF_2COMn(CO)_5 + 2NaCl}$$

$$\mathrm{(CO)_5MnCOCF_2CF_2CF_2COMn(CO)_5 \xrightarrow{105^\circ} (CO)_5MnCF_2CF_2CF_2Mn(CO)_5 + 2CO} \quad (21)^{43}$$

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(42) R. B. King, *J. Amer. Chem. Soc.*, **85**, 1922 (1963).

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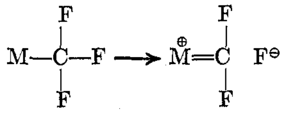
(44) W. Beck, W. Hieber, and H. Tengler, *Ber.*, **94**, 862 (1961).

the ^{19}F nmr spectrum of the binuclear derivative $(CO)_5MnCF_2CF_2CF_2Mn(CO)_5$ exhibits the expected two resonances in a 2:1 relative intensity ratio rather than an anomalous 1:1:1 pattern like the enigmatic hydrogen analog $(CH_2)_3[Mn(CO)_5]_2$ discussed above.

The metal–carbon bond in perfluoroalkylmetal carbonyl derivatives is much stronger than the metal–carbon bond in their hydrogen analogs. This strengthening of the metal–carbon bond in perfluoroalkylmetal carbonyl derivatives may be attributed to the contribution of "no-bond" resonance structures such as the following for trifluoromethyl derivatives.[29,45]



$$M\text{—}CF_3 \longrightarrow \overset{\oplus}{M}\text{=}CF_2 \quad F^{\ominus}$$

The concomitant weakening of the carbon–fluorine bonds in perfluoroalkylmetal carbonyl derivatives is demonstrated by the following observations: (a) lowering of the ν(CF) infrared frequencies sometimes by as much as ~150 cm^{-1} (as in the CF_3 derivatives) relative to derivatives of the same fluorocarbon system not bonded to a transition metal;[29,45] (b) relatively long carbon–fluorine distances found in X-ray crystallographic studies;[46] (c) relative ease of removal of fluorine by basic reagents.[47] To date it has not been possible to find preparative applications of the relative weakness of the carbon–fluorine bond in perfluoroalkyl derivatives of transition metals. The increased strength of the metal–carbon bond of perfluoroalkyl derivatives of transition metals relative to nonfluorinated alkyl derivatives may be dramatic: *e.g.*, $CH_3Co(CO)_4$ as mentioned decomposes above −35° while its fluorine analog, $CF_3Co(CO)_4$, is a liquid stable enough to survive distillation at atmospheric pressure at about 90°.

Metal carbonyl anions are also useful for the synthesis of perfluoroaryl derivatives of certain transition metals, particularly iron. Hexafluorobenzene reacts readily with the very nucleophilic $NaFe(CO)_2C_5H_5$ to give the pentafluorophenyl derivative $C_6F_5Fe(CO)_2C_5H_5$ (XII, X = F) according to eq 22.[48]

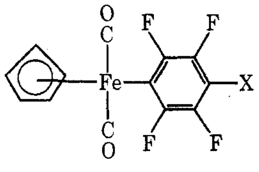
$$NaFe(CO)_2C_5H_5 + C_6F_6 \longrightarrow C_6F_5Fe(CO)_2C_5H_5 + NaF \quad (22)$$

Other highly fluorinated aromatic compounds undergo similar reactions with the very nucleophilic $NaFe(CO)_2C_5H_5$. In the cases of most pentafluorobenzene derivatives of the type C_6F_5X the $Fe(CO)_2C_5H_5$ group enters para to the X group as shown unambiguously by ^{19}F nmr studies on the products; thus octafluorotoluene, $C_6F_5CF_3$, reacts with $NaFe(CO)_2C_5H_5$ to give *p*-$CF_3C_6F_4Fe(CO)_2C_5H_5$ (XII, X = CF_3).[48] Attempts to prepare pentafluorophenyl derivatives of metals other than iron using the reaction between hexafluorobenzene and various metal carbonyl anions were only successful in the case of the preparation of the rhenium derivative $C_6F_5Re(CO)_5$ from hexafluorobenzene and the relatively nucleophilic $NaRe(CO)_5$.[49] No pentafluorophenyl transition metal derivatives were obtained from hexafluorobenzene and the sodium salts $NaMn(CO)_5$, $NaM(CO)_3C_5H_5$ (M = Mo or W), and $NaCo(CO)_4$, all of which contain anions of relatively low nucleophilicity.

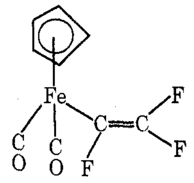
The very nucleophilic $NaFe(CO)_2C_5H_5$ is also useful for the preparation of perfluoroalkenyliron derivatives by reaction with highly fluorinated olefins. Thus the trifluorovinyl derivative $CF_2{=}CFFe(CO)_2C_5H_5$ (XIII) can be prepared from $NaFe(CO)_2C_5H_5$ and tetrafluoroethylene according to eq 23.[49]

$$NaFe(CO)_2C_5H_5 + CF_2{=}CF_2 \xrightarrow{\text{THF}} CF_2{=}CFFe(CO)_2C_5H_5 + NaF \quad (23)$$

Reactions of this type appear to be restricted mainly to the very nucleophilic metal carbonyl anions such as $C_5H_5Fe(CO)_2^-$ and $Re(CO)_5^-$; many related compounds have been prepared by Stone and coworkers.[50]



XII



XIII

Syntheses of Silicon, Germanium, Tin, and Lead Derivatives of Transition Metals

The synthesis of a variety of derivatives with transition metal–carbon σ bonds has given impetus to the synthesis of related compounds with σ bonds between transition metals and the heavier congeners of carbon: silicon, germanium, tin, and lead. In the cases of the germanium, tin, and lead derivatives simple displacement of halide from appropriate organometallic halides using sodium salts of metal carbonyl anions provides a facile preparation of many such compounds in high yield, *e.g.*, eq 24.[51,52]

$$NaMn(CO)_5 + R_3ECl \xrightarrow{\text{THF}} R_3EMn(CO)_5 + NaCl \quad (24)$$

$$E = Ge, Sn, \text{ and } Pb; \quad R = \text{methyl, phenyl, etc.}$$

Indeed the facile and efficient reactions of trialkyltin halides with many metal carbonyl anions are sometimes useful for the identification of such anions in unknown solutions. In the case of the organosilicon chlorides only the very nucleophilic sodium salt $NaFe(CO)_2C_5H_5$ gives good yields of transition metal–silyl derivatives when the reaction is run in tetrahydrofuran solution under normal conditions. Indeed some rather unusual organosilyliron derivatives can be prepared from organosilicon halides and $NaFe(CO)_2C_5H_5$, *e.g.*,[53] eq 25. The ν(Si–H) frequency of the

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(45) F. A. Cotton and R. M. Wing, *J. Organometal Chem.*, **9**, 511 (1967).

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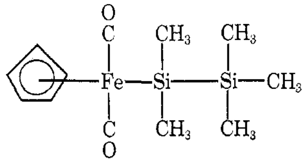
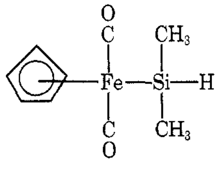
$$\mathrm{NaFe(CO)_2C_5H_5 + (CH_3)_3SiSi(CH_3)_2Cl \xrightarrow{THF} \underset{XIV}{(CH_3)_3SiSi(CH_3)_2Fe(CO)_2C_5H_5} + NaCl} \quad (25a)$$

$$\mathrm{NaFe(CO)_2C_5H_5 + (CH_3)_2Si(H)Cl \xrightarrow{THF} \underset{XV}{(CH_3)_2Si(H)Fe(CO)_2C_5H_5} + NaCl} \quad (25b)$$

dimethylsilyliron compound XV occurs at the relatively low value of 2071 $\mathrm{cm^{-1}}$, but the relatively low electronegativity of the iron atom in the $\mathrm{C_5H_5Fe(CO)_2}$ substituent on the silicon atom is sufficient to account for this shift.



XIV



XV

Attempts to prepare organosilyl derivatives of transition metals using sodium salts other than the very nucleophilic $\mathrm{NaFe(CO)_2C_5H_5}$ have been uniformly unsuccessful in cases where reactions were carried out in tetrahydrofuran solution in the normal manner. However, a few such reactions between silyl halides and metal carbonyl anions of appreciably lower nucleophilicity than $\mathrm{C_5H_5Fe(CO)_2^-}$ have been successful when solvents less basic than tetrahydrofuran were used, *e.g.*, eq 26 and 27.

$$\mathrm{NaCo(CO)_4 + SiH_3I \xrightarrow{(C_2H_5)_2O} SiH_3Co(CO)_4 + NaI} \quad (26)[54]$$

$$\mathrm{NaMn(CO)_5 + (CH_3)_3SiCl \xrightarrow[\text{no solvent}]{} (CH_3)_3SiMn(CO)_5 + NaCl} \quad (27)[55]$$

Basic solvents apparently cleave the metal–silicon bond in all transition metal silyl derivatives except those derived from the extremely nucleophilic $\mathrm{C_5H_5Fe(CO)_2^-}$, as exemplified by reaction 28.[56] Tetrahydrofuran and many other basic solvents are thus sufficiently strong Lewis bases to displace all metal carbonyl anions except the very nucleophilic $\mathrm{C_5H_5Fe(CO)_2^-}$ from their adducts with $\mathrm{R_3Si^+}$ cations (*i.e.*, $\mathrm{R_3Si}$ derivatives of metal carbonyls).

$$\mathrm{R_3SiCo(CO)_4 + R'_3N \longrightarrow [R'_3N\text{-}SiR_3]^+[Co(CO)_4]^-} \quad (28)$$

The transition metal derivatives of silicon and its heavier congeners are much more stable than analogous transition metal derivatives of carbon. Compounds like $\mathrm{H_3SiCo(CO)_4}$ and $\mathrm{(CH_3)_3SnCo(CO)_4}$ are stable at temperatures above +100°.[54,57] This increase in stability may be attributed to the presence of empty d orbitals on silicon and its heavier congeners which lead to some partial $d\pi$–$d\pi$ double bonding between these empty orbitals and the filled d orbitals of the transition metal.

π-Allylic and Related Compounds from Metal Carbonyl Anions

The simplest example of a decarbonylation reaction in which a one-electron donor ligand[23] becomes a three-electron donor ligand is the preparation of π-allyl derivatives from allyl halides and metal carbonyl anions. Heck and Breslow[58] first reported a reaction of this type. They found that $\mathrm{NaCo(CO)_4}$ and allyl bromide reacted readily with carbon monoxide evolution to give the π-allyl derivative $\mathrm{C_3H_5Co(CO)_3}$ (XVI), according to eq 29. This π-allyl derivative (XVI) is stable above room temperature.

$$\mathrm{NaCo(CO)_4 + CH_2{=}CHCH_2Br \longrightarrow C_3H_5Co(CO)_3 + NaBr + CO} \quad (29)$$

Study of the allyl derivatives of the manganese carbonyl system clarified considerably the course of reactions of this type.[59,60] Allyl chloride reacts with $\mathrm{NaMn(CO)_5}$ in tetrahydrofuran at room temperature to give a yellow air-sensitive liquid, $\mathrm{C_3H_5Mn(CO)_5}$, according to eq 30. On the basis of its nmr spectrum this liquid was formulated as the σ-allyl derivative XVII in which the allyl group is bonded to the manganese atom through only one carbon atom. The compound $\mathrm{C_3H_5Mn(CO)_5}$ (XVII) is thus closely related to the methyl derivative $\mathrm{CH_3Mn(CO)_5}$. If the liquid $\mathrm{C_3H_5Mn(CO)_5}$ (XVII) is heated to 80° in a sealed evacuated tube, it loses 1 mole of carbon monoxide to form the yellow crystalline π-allyl derivative $\mathrm{C_3H_5Mn(CO)_4}$ (XVIII), *i.e.*

$$\mathrm{NaMn(CO)_5 + CH_2{=}CHCH_2Cl \xrightarrow{THF} CH_2{=}CHCH_2Mn(CO)_5 + NaCl} \quad (30)$$

$$\mathrm{\underset{XVII}{C_3H_5Mn(CO)_5} \longrightarrow \underset{XVIII}{C_3H_5Mn(CO)_4} + CO}$$

In $\mathrm{C_3H_5Mn(CO)_4}$ (XVIII) the allyl group is bonded to the manganese atom through all three carbon atoms, as in the cobalt derivative $\mathrm{C_3H_5Co(CO)_3}$ (XVI) discussed above. The formation of the cobalt derivative $\mathrm{C_3H_5Co(CO)_3}$ (XVI) directly from $\mathrm{NaCo(CO)_4}$ and an allyl halide at room temperature is a further indication of the greater ease of decarbonylation of $\mathrm{RCo(CO)_4}$ derivatives relative to analogous $\mathrm{RMn(CO)_5}$ derivatives.

Since the discovery of the first π-allyl metal carbonyls of cobalt and manganese as described above, numerous other π-allylic metal carbonyl derivatives have been prepared. Of particular significance is the π-benzyl derivative $\mathrm{C_6H_5CH_2Mo(CO)_2C_5H_5}$ (XIX)[61] since this was one of the earliest fluxional[62] organometallic com-

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[60] W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, **83**, 1601 (1961).

[61] R. B. King and A. Fronzaglia, *ibid.*, **88**, 709 (1966).

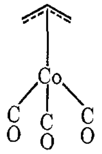
[62] F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

pounds to be positively identified from a temperature-dependence study of its nmr spectrum. This π-benzyl derivative was prepared by the reaction sequence[61] eq 31, 32. In this case the decarbonylation reaction

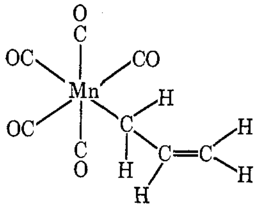
$$\mathrm{NaMo(CO)_3C_5H_5 + C_6H_5CH_2Cl \xrightarrow{THF} \underset{\text{XX (yellow)}}{C_6H_5CH_2Mo(CO)_3C_5H_5} + NaCl} \quad (31)$$

$$\mathrm{C_6H_5CH_2Mo(CO)_3C_5H_5 \xrightarrow[\text{uv}]{\Delta \text{ or}} \underset{\text{XIX (red)}}{C_6H_5CH_2Mo(CO)_2C_5H_5} + CO} \quad (32)$$

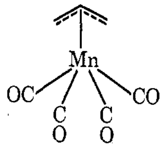
yields less than 10% $C_6H_5CH_2Mo(CO)_2C_5H_5$ and is accompanied by the formation of relatively large amounts of by-products such as $[C_5H_5Mo(CO)_3]_2$. The nmr spectrum of $C_6H_5CH_2Mo(CO)_2C_5H_5$ at −40° was consistent with a "fixed" structure such as XIXa with all seven protons of the π-benzyl ligand nonequivalent. However, at elevated temperatures (*e.g.*, +65°) three pairs of the π-benzyl protons coalesced into a 1:2:2:2 pattern, indicating rapid interchange between equivalent structures XIXa and XIXb. Subsequent more detailed work[63] has been done on this system and related fluxional molecules, but a discussion of this work is beyond the scope of this Account.



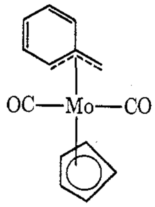
XVI



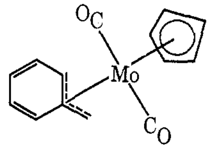
XVII



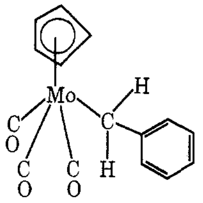
XVIII



XIXa



XIXb

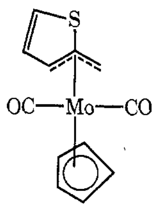


XX

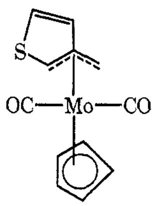
The π-benzyl derivative $C_6H_5CH_2Mo(CO)_2C_5H_5$ (XIX) may be considered as derived from a π-allyl derivative with a benzene ring fused to the π-allyl ligand. The fact that the formation of a π-benzyl derivative "interferes" with the aromaticity of the benzene ring may account for the relatively low yield in the above preparation.

The unusual fluxional behavior of the π-benzyl derivative $C_6H_5CH_2Mo(CO)_2C_5H_5$ (XIX) has prompted the synthesis of related π-allylic derivatives with other aromatic systems fused to the π-allyl system. This led to the synthesis of the two isomeric π-thenyl derivatives $C_4H_3SCH_2Mo(CO)_2C_5H_5$ (XXI and XXII) by a procedure completely analogous to the synthesis of the π-benzyl derivative $C_6H_5CH_2Mo(CO)_2C_5H_5$ (XIX) except for a much higher yield (30–55%) in the decarbonylation step.[64] Neither π-thenyl derivative XXI nor XXII exhibited any nmr evidence for fluxional properties in the temperature range −60 to +110°. However, in the case of neither π-thenyl derivative XXI or XXII is it possible to draw two equivalent interchangeable structures comparable to XIXa and XIXb for the π-benzyl derivative.

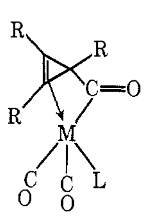
Some reactions between metal carbonyl anions and cyclopropenyl cations have been investigated in attempts to prepare π-cyclopropenyl derivatives. Coffey[65] first reported the reaction of triphenylcyclopropenyl bromide with the sodium salts $NaCo(CO)_4$ and $NaFe(CO)_3NO$ to give the derivatives $(C_6H_5)_3C_3COCo(CO)_3$ and $(C_6H_5)_3C_3COFe(CO)_2NO$, respectively. He formulated these compounds as the cyclopropenylcarbonyl derivatives XXIII (R = C_6H_5, M = Co, L = CO; R = C_6H_5, M = Fe, L = NO). Much more recently[66] the related compound $(CH_3)_3C_3COCo(CO)_3$ was prepared from trimethylcyclopropenyl tetrafluoroborate and $NaCo(CO)_4$. Spectroscopic evidence, particularly the nmr chemical shifts of the methyl protons, suggested formulation of $(CH_3)_3C_3COCo(CO)_3$ as the ketocyclobutenyl derivative XXIV (R = CH_3, M = Co, L = CO) rather than as the cyclopropenylcarbonyl derivative XXIII (R = CH_3, M = Co, L = CO). The obvious similarities in the properties, particularly the ν(CO) frequencies, of $(CH_3)_3C_3COCo(CO)_3$ and those of Coffey's compounds $(C_6H_5)_3C_3COCo(CO)_3$ and $(C_6H_5)_3C_3COFe(CO)_2NO$ suggest that the latter compounds are also ketocyclobutenyl derivatives XXIV (R = C_6H_5, M = Co, L = CO; R = C_6H_5, M = Fe, L = NO). Reactions of metal carbonyl anions with cyclopropenyl cations to date have not been successful for the preparation of π-cyclopropenylmetal carbonyl derivatives, although such compounds have been obtained by other synthetic routes.[67,68] Furthermore, reactions of cyclopropenyl cations with metal carbonyls, forming $RM(CO)_n(C_5H_5)_m$ derivatives which decarbonylate only with difficulty (*e.g.*, $NaFe(CO)_2C_5H_5$ and $NaMo(CO)_3C_5H_5$), have not yielded metal carbonyl derivatives incorporating the three-membered ring system.



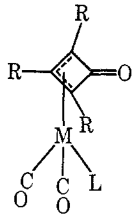
XXI



XXII



XXIII



XXIV

Reactions of Certain Organosulfur and Organonitrogen Derivatives with Metal Carbonyl Anions

The preparation of π-allylic and related metal car-

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(63) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 1339 (1969).

(64) R. B. King and R. N. Kapoor, *Inorg. Chem.*, **8**, 2535 (1969).

(65) C. E. Coffey, *J. Amer. Chem. Soc.*, **84**, 118 (1962).

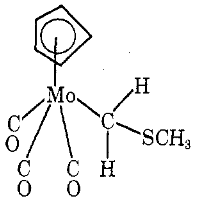
(66) R. B. King and A. Efraty, *J. Organometal. Chem.*, **24**, 241 (1970).

(67) R. G. Hayter, *ibid.*, **13**, P1 (1968).

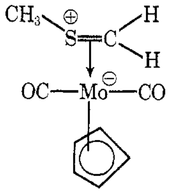
(68) E. W. Gowling and S. F. A. Kettle, *Inorg. Chem.*, **3**, 604 (1964).

bonyl derivatives by decarbonylation of the corresponding σ-allylic metal carbonyl derivatives indicates that electron pairs from carbon–carbon double bonds (including those in aromatic rings in the cases of π-benzyl and π-thenyl derivatives) can displace carbonyl groups in $RM(CO)_n(C_5H_5)_m$ derivatives. This suggested the study of the decarbonylation of other $RM(CO)_n(C_5H_5)_m$ derivatives where the R group contains a potential electron-pair donor. This led to an investigation of reactions of metal carbonyl anions with haloalkyl sulfides[69,70] and haloalkylamines.[71]

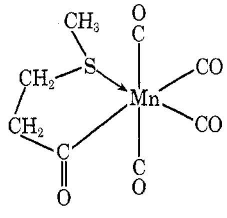
Several different reactions of metal carbonyl anions with chloromethyl methyl sulfide, $ClCH_2SCH_3$, were investigated.[69,70] Thus the reaction of the sodium salt $NaMo(CO)_3C_5H_5$ with chloromethyl methyl sulfide proceeds in the normal manner to give the yellow crystalline σ-alkyl derivative $CH_3SCH_2Mo(CO)_3C_5H_5$ of structure XXV with no molybdenum–sulfur bond. Compound XXV loses 1 mole of carbon monoxide upon ultraviolet irradiation or heating to 70° to give the likewise yellow crystalline dicarbonyl $CH_3SCH_2Mo(CO)_2C_5H_5$. The nmr spectrum suggested structure XXVI for this dicarbonyl complex, and this was subsequently confirmed by X-ray crystallography.[71] In structure XXVI the CH_3SCH_2 group is bonded to the molybdenum atom by both molybdenum–carbon and molybdenum–sulfur bonds. The CH_3SCH_2 group bonded to a metal atom as in $CH_3SCH_2Mo(CO)_2C_5H_5$ (XXVI) has a similar relationship to π-allylic compounds as thiophene has to benzene. Other known derivatives with a CH_3SCH_2 group bonded to a metal atom as in the molybdenum complex $CH_3SCH_2Mo(CO)_2C_5H_5$ (XXVI) include the orange crystalline tungsten analog $CH_3SCH_2W(CO)_2C_5H_5$ and the yellow liquid manganese derivative $CH_3SCH_2Mn(CO)_4$.[72]



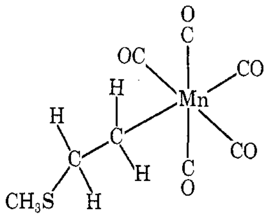
XXV



XXVI



XXVII



XXVIII

The reactions of metal carbonyl anions with 2-chloroethyl methyl sulfide, $ClCH_2CH_2SCH_3$, are entirely different from the reactions of metal carbonyl anions with chloromethyl methyl sulfide discussed above.[69,70] Reaction of $NaMn(CO)_5$ with 2-chloroethyl methyl sulfide gives a yellow crystalline product of the expected composition $CH_3SCH_2CH_2Mn(CO)_5$ for a "normal" σ-alkyl derivative. However, the infrared spectrum of this compound exhibits a strong acyl carbonyl frequency at 1631 cm^{-1} as well as terminal ν(CO) frequencies in appropriate positions for a *cis*-$Mn(CO)_4$ group, indicating that this product is the cyclic acyl derivative XXVII. The formation of this cyclic acyl derivative from $NaMn(CO)_5$ and $ClCH_2CH_2SCH_3$ probably proceeds through an intermediate $CH_3SCH_2CH_2Mn(CO)_5$ (XXVIII) with the $CH_3SCH_2CH_2$ group bonded to the manganese atom only through a manganese–carbon σ bond. The sulfur atom in $CH_3SCH_2CH_2Mn(CO)_5$ (XXVIII) can act as a Lewis base and displace one of the carbonyl groups in the $Mn(CO)_5$ group. The displaced carbon monoxide can then insert into the manganese–carbon σ bond to the $CH_3SCH_2CH_2$ group, thereby resulting in the observed cyclic acyl derivative XXVII. Such a reaction represents an intramolecular version of reaction 33, reported by Keblys and Filbey[73] in 1960. Further

$$CH_3Mn(CO)_5 + R_3N \longrightarrow CH_3COMn(CO)_4NR_3 \qquad (33)$$

evidence for this proposed mechanism for the reaction between $NaMn(CO)_5$ and 2-chloroethyl methyl sulfide comes from a study of the analogous reaction between $NaFe(CO)_2C_5H_5$ and 2-chloroethyl methyl sulfide.[70] The latter reaction when carried out in tetrahydrofuran solution at room temperature gives the yellow-brown liquid $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ (XXIX) analogous to $CH_3SCH_2CH_2Mn(CO)_5$ (XXVIII). Ultraviolet irradiation of $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ (XXIX) results in the conversion of some of this material into the red crystalline isomeric cyclic acyl derivative $CH_3SCH_2CH_2COFeCOC_5H_5$ (XXX). The isomers XXIX and XXX, besides having widely different colors and melting points, also have very different infrared ν(CO) frequencies in accord with their structures. Thus the isomer XXIX exhibits two terminal ν(CO) frequencies (1990 and 1930 cm^{-1}) and no acyl ν(CO) frequencies similar to other $RFe(CO)_2C_5H_5$ derivatives. The isomer XXX, on the other hand, exhibits only one terminal ν(CO) frequency (1935 cm^{-1}) as well as one acyl ν(CO) frequency (1618 cm^{-1}).

The yield in the photochemical isomerization of XXIX to XXX is only about 5%.[70] In this photolysis reaction a larger quantity of the starting $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ (XXIX) is converted to brown $CH_3SFe(CO)_2C_5H_5$ (XXXI), apparently by elimination of ethylene according to eq 34. The preparation of $CH_3SFe(CO)_2C_5H_5$ (XXXI) at that time represented the first reported example of a metal carbonyl derivative with a terminal rather than a bridging alkylthio group.

$$CH_3SCH_2CH_2Fe(CO)_2C_5H_5 \xrightarrow{uv} CH_3SFe(CO)_2C_5H_5 + CH_2{=}CH_2 \qquad (34)$$

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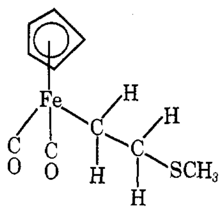
[69] R. B. King and M. B. Bisnette, *J. Amer. Chem. Soc.*, **86**, 1267 (1964).

[70] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 486 (1965).

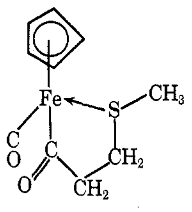
[71] E. R. de Gil and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 3751 (1969).

[72] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 482 (1965).

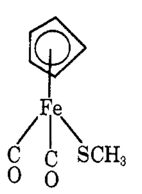
[73] K. A. Keblys and A. H. Filbey, *J. Amer. Chem. Soc.*, **82**, 4204 (1960).



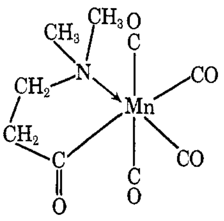
XXIX



XXX



XXXI

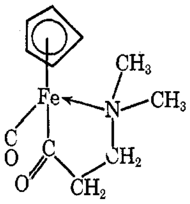


XXXII

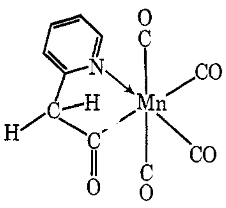
Subsequently more convenient and efficient preparations of $CH_3SFe(CO)_2C_5H_5$ were found using either the room temperature reaction of $HFe(CO)_2C_5H_5$ with dimethyl disulfide or the room temperature photolysis of $[C_5H_5Fe(CO)_2]_2$ with dimethyl disulfide.[72]

Some reactions of metal carbonyl anions with the amine derivative $(CH_3)_2NCH_2CH_2Cl$ were investigated in order to ascertain whether a lone pair on a nitrogen atom could behave like a lone pair on a sulfur atom in forming cyclic acyl derivatives.[74] The reaction between $NaMn(CO)_5$ and $(CH_3)_2NCH_2CH_2Cl$ was found to give the yellow crystalline cyclic acyl derivative $(CH_3)_2NCH_2CH_2COMn(CO)_4$ (XXXII) closely related to the sulfur derivative $CH_3SCH_2CH_2COMn(CO)_4$ (XXVII) discussed above. The red crystalline iron cyclic acyl derivative $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ (XXXIII) could be prepared in low yield from $NaFe(CO)_2C_5H_5$ and $(CH_3)_2NCH_2CH_2Cl$. However, the reactivity of $(CH_3)_2NCH_2CH_2Cl$, like that of $CH_3SCH_2CH_2Cl$, was too low to form similar derivatives with the sodium salts $NaM(CO)_3C_5H_5$ (M = Mo and W).

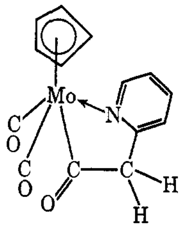
A much more reactive halide than $(CH_3)_2NCH_2CH_2Cl$ which also forms cyclic acyl derivatives is 2-chloromethylpyridine.[74] Reaction of 2-chloromethylpyridine with $NaMn(CO)_5$ forms the yellow crystalline cyclic acyl derivative $NC_5H_4CH_2COMn(CO)_4$ (XXXIV) similar to the cyclic acyl derivatives obtained from $NaMn(CO)_5$ and $(CH_3)_2NCH_2CH_2Cl$ or $CH_3SCH_2CH_2Cl$. However, among the three halides investigated, 2-chloromethylpyridine is the only one which is reactive enough to form a cyclic acyl derivative with the sodium salt $NaMo(CO)_3C_5H_5$; in this case the product is $NC_5H_4CH_2COMo(CO)_2C_5H_5$ (XXXV). Interestingly enough, the tungsten analog $NaW(CO)_3C_5H_5$ reacts with 2-chloromethylpyridine to form a normal alkyltungsten derivative $NC_5H_4CH_2W(CO)_3C_5H_5$ (XXXVI) rather than a cyclic acyl derivative analogous to $NC_5H_4CH_2COMo(CO)_2C_5H_5$ (XXXV). Formation of a cyclic acyl derivative such as XXVII, XXX, XXXII, XXXIII, XXXIV, or XXXV requires rupture of a metal–carbon bond. The increased stability of tungsten–carbon bonds relative to molybdenum–carbon bonds[75] can account for the observation that $NaMo(CO)_3C_5H_5$ but not $NaW(CO)_3C_5H_5$ forms a cyclic acyl derivative with 2-chloromethylpyridine just as it accounts for the greater ease of decarbonylation of $RCOMo(CO)_3C_5H_5$ derivatives relative to $RCOW(CO)_3C_5H_5$ derivatives, as discussed earlier in this Account.



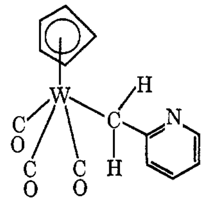
XXXIII



XXXIV



XXXV



XXXVI

Conclusion

Metal carbonyl anions are a useful class of nucleophiles which react with a variety of halides and other electrophilic reagents. From such reactions a wide variety of novel metal carbonyl derivatives can be obtained. Some of these derivatives such as the arylazo, CH_3SCH_2, and cyclic acyl derivatives exhibit unusual types of chemical bonding. Other of these derivatives have interesting chemical and spectroscopic properties. Further study of this area of chemistry is likely to lead to significant progress both in fundamental chemistry and in areas of practical importance such as catalysis.

I am indebted to the Air Force Office of Scientific Research for support of much of this research in this area, particularly during the period 1964–1966 at the Mellon Institute (now Carnegie-Mellon University). I also acknowledge the contributions of my coworkers indicated in the references, particularly the contributions of Mr. M. B. Bisnette during 1962–1966.

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(74) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 293 (1966).

(75) R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969)