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PERSPECTIVES IN THE SYNTHESES OF NOVEL ORGANOMETALLIC COMPOUNDS USING METAL CARBONYL ANIONS

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In 1956 during my senior year of undergraduate study at Oberlin College in Ohio in preparation for medical school and a career in medicine like that of my father, I first became aware of the intriguing discovery of ferrocene several years earlier by Kealy and Pauson [1] and by Miller, Tebboth, and Tremaine [2] and the subsequent development of the chemistry of cyclopentadienyl-metal derivatives in the laboratories of Wilkinson at Harvard and of Fischer in Munich. My interest in this area developed to the extent that within a period of weeks I abandoned my plans to attend medical school and instead applied to various graduate schools in chemistry. I was admitted to Harvard and after a summer at American Cyanamid in Stamford, Connecticut, attempting to synthesize unusual organophosphorus compounds, I entered Harvard in fall 1957. By that time Professor Wilkinson had left Harvard to take a professorship at Imperial College in London but Professor F.G.A. Stone, then at Harvard, had become interested in expanding his research programs to include transition metal organometallic chemistry and thus agreed to allow me to work in this area of chemistry for my doctorate.

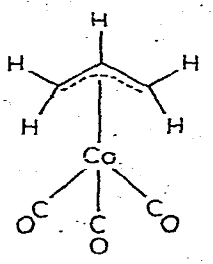
Much of this work during my graduate career at Harvard involved a study of the reactions of various unsaturated organic compounds with metal carbonyls. However, another problem of interest to us at this time was the preparation of perfluoroalkyl-transition metal derivatives, a class of compounds unknown at that time.

In 1957 Closson, Kozikowski, and Coffield [3] had reported that $NaMn(CO)_5$, preparable from $Mn_2(CO)_{10}$ and dilute sodium amalgam, reacted with methyl iodide to give the very stable $CH_3Mn(CO)_5$. They had also established that $NaMn(CO)_5$ reacted with acetyl chloride to give the isolable acetyl derivative $CH_3COMn(CO)_5$, which underwent decarbonylation on mild heating to give $CH_3Mn(CO)_5$. Furthermore, Piper, and Wilkinson [4], in what must now be regarded as one of the classic papers in transition metal organometallic chemistry, had developed the preparations of $NaFe(CO)_2C_5H_5$ from $[C_5H_5Fe(CO)_2]_2$ and dilute sodium amalgam and of $NaM(CO)_3C_5H_5$ (M = Mo and W) from $M(CO)_6$ (M = Mo and W) and sodium cyclopentadienide and used these then novel reagents to prepare the equally novel methyl derivatives $CH_3Fe(CO)_2C_5H_5$ and

$CH_3M(CO)_3C_5H_5$ (M = Mo and W). The tungsten derivative $CH_3W(CO)_3C_5H_5$ had also been discovered independently by Fischer, Hafner, and Stahl [5].

An obvious method for the preparation of perfluoroalkylmetal carbonyls might have been the reactions of these sodium salts of metal carbonyl anions with perfluoroalkyl halides. However, the strong inductive effect of the fluorines in perfluoroalkyl iodides, R_fI, the most readily available perfluoroalkyl halides, was known [6] to make the iodine in these compounds positive and the perfluoroalkyl groups negative. This suggested that reactions of metal carbonyl anions with perfluoroalkyl iodides would give metal carbonyl iodides rather than the desired perfluoroalkylmetal carbonyls. We therefore avoided this synthetic approach and instead treated perfluoroacyl chlorides R_fCOCl ($R_f = C_2F_5$ and n-C_3F_7) with the sodium pentacarbonylmetallates $NaM(CO)_5$ (M = Mn and Re) to give the corresponding perfluoroacylmetal carbonyls $R_fCOM(CO)_5$, which underwent decarbonylation upon heating to give the desired perfluoroalkylmetal carbonyls $R_fM(CO)_5$ [7]. Similar independent discoveries of perfluoroalkylmetal carbonyls were made almost concurrently by McClellan of Dupont [8] and Beck, Hieber and Tengler in Munich [9] as well as by Closson, Kozikowski, and Coffield [10]. During that period we also found that the iron—iron bonds in $Fe_3(CO)_{12}$ could be cleaved with sodium metal in boiling tetrahydrofuran to give a solution of $Na_2Fe(CO)_4$ which reacted with the perfluoroacyl halides R_fCOCl ($R_f = C_2F_5$ and n-C_3F_7) to give directly the corresponding perfluoroalkyliron carbonyls $(R_f)_2Fe(CO)_4$ without isolation of the intermediate perfluoroacyl derivatives [11]. Several years later, I successfully used a modification of this synthetic approach to prepare perfluoroalkyl derivatives of the cyclopentadienylmetal carbonyls of the general types $R_fMo(CO)_3C_5H_5$ and $R_fFe(CO)_2C_5H_5$ [12].

Another significant discovery in transition metal organometallic chemistry during my graduate school days at Harvard was the observation by Heck and Breslow [13] that allyl chloride reacts with $NaCo(CO)_4$ to give allylcobalt tricarbonyl, $C_3H_5Co(CO)_3$, rather than allylcobalt tetracarbonyl, $C_3H_5Co(CO)_4$, analogous to the very unstable [14] $CH_3Co(CO)_4$. The spectroscopic properties and relative stability of this allylcobalt tricarbonyl led to the formulation of this as I in which the allyl group is what would now be known as a *trihapto*-allyl ligand [15].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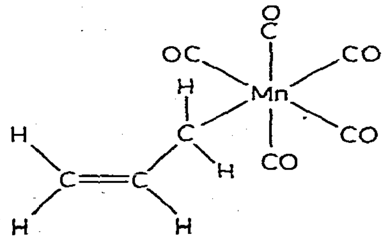
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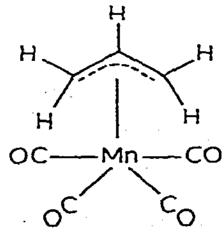
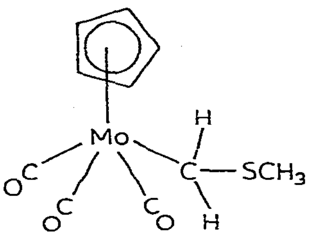

(III)

Shortly after reading about the discovery of allylcobalt tricarbonyl, I arrived at the prediction that the manganese carbonyl system should form not only an analogous allylmanganese tetracarbonyl with a *trihapto*-allyl ligand but also a stable allylmanganese pentacarbonyl with a *monohapto*-allyl ligand, since $CH_3Mn(CO)_5$, in contrast to $CH_3Co(CO)_4$ [14], is a relatively stable compound [3]. Experiment verified this prediction perfectly, since we found allyl chloride to react with $NaMn(CO)_5$ to give a good yield of the yellow liquid *monohapto*-allyl derivative $C_3H_5Mn(CO)_5$ (II) which underwent smooth decarbonylation upon mild heating to form the yellow crystalline *trihapto*-allyl derivative $C_3H_5Mn(CO)_4$ (III) [16].

During the period 1962-1966 while at the Mellon Institute in Pittsburgh, Pennsylvania, I had the opportunity to develop further the metal carbonyl anions as reagents for the preparation of unusual organometallic compounds. At that time one idea was the replacement of a —CH=CH— unit in a *trihapto*-allyl group in derivatives such as I and III with a sulfur atom similar to the substitution of —CH=CH— in benzene with sulfur to give thiophene. This led to an investigation of the reactions of the halide CH_3SCH_2Cl with various metal carbonyl anions; the methyl substituent on sulfur was used to avoid possible interfering reactions of a thiol group. Reaction of CH_3SCH_2Cl with $NaMo(CO)_3C_5H_5$ at room temperature gave a yellow crystalline solid $CH_3SCH_2Mo(CO)_3C_5H_5$ formulated as the *monohapto*-derivative IV [17]. Mild heating or ultraviolet irradiation of IV gave a different yellow solid, with a nearly identical melting point. Elemental analyses combined with infrared and proton NMR spectra indicated this second yellow solid to be the dicarbonyl $CH_3SCH_2Mo(CO)_2C_5H_5$ (V) with a *dihapto*-CH_3SCH_2 group. This structure V was eventually confirmed by X-ray crystallography [18]. A similar yellow liquid manganese carbonyl derivative $CH_3SCH_2Mn(CO)_4$ (VI) was also prepared, but the corresponding cobalt carbonyl derivative, unlike I, appeared to be too unstable for isolation.



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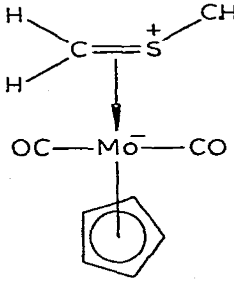

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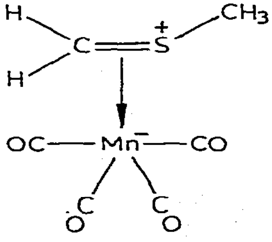
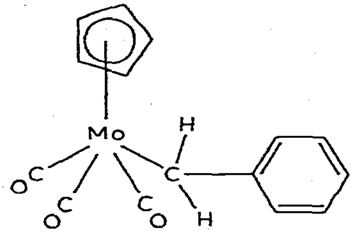


(VI).

The proton NMR spectra provided an excellent means for differentiating between *monohapto*- and *dihapto*-CH_3SCH_2 groups since the two CH_2 protons in the former type of compounds (e.g. IV) are equivalent and appear as a singlet whereas the two CH_2 protons in the *dihapto*-CH_3SCH_2 derivatives (e.g. V and VI) are non-equivalent and thus appear as a pair of *AB* doublets.

Another interesting modification of the *trihapto*-allyl group as found in I and III is the fusion of a benzene ring to give a *trihapto*-benzyl group. Reaction of benzyl chloride with $NaMo(CO)_3C_5H_5$ was found to give the yellow *monohapto*-benzyl derivative $C_6H_5CH_2Mo(CO)_3C_5H_5$ (VII) [19]. Pyrolysis or photolysis of this *monohapto*-benzyl derivative gave $[C_5H_5Mo(CO)_3]_2$ as the principal product; however, decarbonylation to give the red dicarbonyl $C_6H_5CH_2Mo(CO)_2$-



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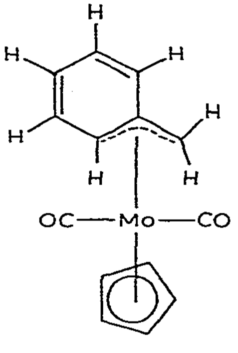

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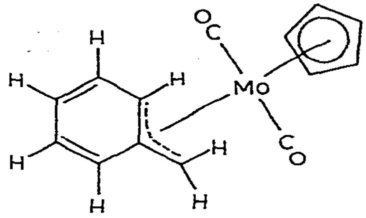
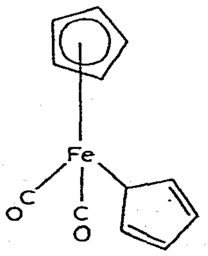


(VIIIb)

C_5H_5 (VIII) also occurred in low yield. In an attempt to provide spectroscopic evidence for the *trihapto*-benzyl structure VIII, the proton NMR spectrum of this compound was investigated. At ambient temperatures this spectrum exhibited the sharp resonance from the five equivalent cyclopentadienyl protons and a broad resonance from the five phenyl protons but no resonance from the methylene protons [19]. The reason for the failure to observe the methylene protons in this NMR spectrum was revealed when the spectrum was run again both above and below temperature: at −40° the NMR spectrum of VIII exhibited the two doublet *AB* pattern for the methylene protons as well as distinct resonances from each of the five non-equivalent phenyl protons in VIII whereas at +64° this spectrum exhibited a sharp singlet for both methylene protons and fewer phenyl proton resonances. Furthermore, the methylene singlet in the high temperature NMR spectrum had a chemical shift corresponding to approximately the mean value of the chemical shifts of the two doublets of the methylene *AB* pattern in the low temperature NMR spectrum. The *trihapto*-benzyl derivative VIII was thus an early example of a fluxional organometallic molecule [20] in which the interconversion between the two equivalent structures VIIIa and VIIIb is slow on the NMR time scale at low temperatures (e.g. −40°) but rapid on the NMR time scale at high temperatures (e.g. +64°), which are still below the decomposition temperature. The *trihapto*-benzyl derivative VIII was among the first fluxional organometallic derivatives for which both the limiting low temperature and the completely equilibrating high temperature NMR spectra were reported although NMR observations indicative of fluxional properties had been made on $C_5H_5Fe(CO)_2C_5H_5$ (IX) as far back as 1956 [4, 21] and on the cyclooctatetraene complex $C_8H_8Fe(CO)_3$ (X) in 1959 [22].



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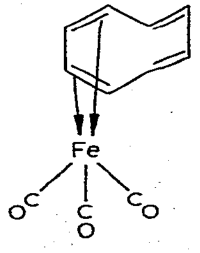

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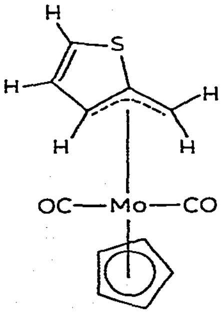

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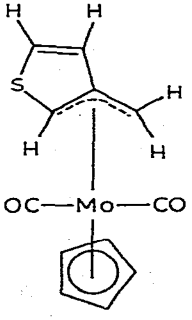
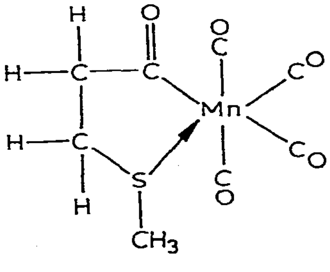


(XII)

Analogous to the fusion of a benzene ring to a *trihapto*-allyl group to give a *trihapto*-benzyl group is the fusion of a thiophene ring to a *trihapto*-allyl group to give the *trihapto*-2-thenyl and 3-thenyl groups. Reactions of 2- and 3-chloromethylthiophenes with $NaMo(CO)_3C_5H_5$ followed by thermal decarbonylation gave the corresponding *trihapto*-thenyl derivatives XI and XII, respectively [23]. These *trihapto*-thenyl derivatives did not exhibit any evidence for fluxional properties in their proton NMR spectra consistent with the absence of two equivalent potentially equilibrating structures corresponding to VIIIa and VIIIb for the *trihapto*-benzyl derivative.

The allyl, benzyl, thenyl, and methylthiomethyl halides used for the syntheses of various complexes cited above are examples of organic halides containing a functional group potentially capable of interacting with transition metal systems. Other organic halides of this general type have given unusual and significant metal complexes upon reactions with metal carbonyl anions. The successful use of CH_3SCH_2Cl for the preparations of the *dihapto*-CH_3SCH_2 derivatives V and VI led to an investigation of reactions of its higher homolog $CH_3SCH_2CH_2Cl$ with metal carbonyl anions [17]. Reaction of $CH_3SCH_2CH_2Cl$ with $NaMn(CO)_5$ gave a yellow crystalline solid of stoichiometry $CH_3SCH_2CH_2Mn(CO)_5$. The infrared spectrum of this product was inconsistent with its formulation as an $RMn(CO)_5$ derivative analogous to $CH_3Mn(CO)_5$ since this product exhibited a strong acyl carbonyl $\nu(CO)$ frequency around 1600 cm^{-1} as well as a pattern of terminal metal carbonyl $\nu(CO)$ frequencies consistent with a *cis*-$L_2M(CO)_4$ structure rather than an $LM(CO)_5$ structure. This led to the formulation of this manganese complex as the cyclic acyl derivative XIII. Reaction of $CH_3SCH_2CH_2Cl$ with $NaFe(CO)_2C_5H_5$ gave an orange-brown liquid $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ shown by its infrared $\nu(CO)$ frequencies to be the normal *monohapto*-derivative XIV. Ultraviolet irradiation of XIV gave a relatively complex mixture of products which could be separated by column chromatography. One of these products, formed in relatively low yields, was the isomeric cyclic acyl derivative XV analogous to XIII. Another product was $CH_3SFe(CO)_2C_5H_5$, of significance at that time for being the first metal carbonyl derivative with terminal rather than bridging alkylthio groups. Later a more convenient preparation of $CH_3SFe(CO)_2C_5H_5$ by the photolysis of $[C_5H_5Fe(CO)_2]_2$ with dimethyl disulfide at room temperature was developed [24].



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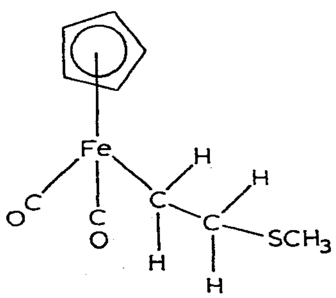

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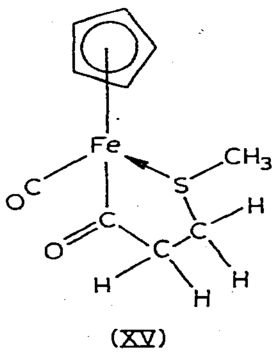
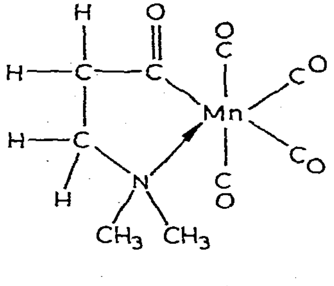


(XV)

Cyclic acyl derivatives similar to XIII and XV were also obtained from haloalkylamines and metal carbonyl anions [25]. Thus the reaction of NaMn-

$(CO)_5$ with $(CH_3)_2NCH_2CH_2Cl$ gave the yellow cyclic acyl derivative $(CH_3)_2NCH_2CH_2COMn(CO)_4$ (XVI) similar to XIII. The reactions of the more reactive 2-chloromethylpyridine with the metal carbonyl anions $NaM(CO)_3C_5H_5$ (M = Mo and W) were particularly interesting since the molybdenum anion gave the cyclic acyl derivative XVII whereas the tungsten anion gave an ordinary *monohapto*-derivative XVIII; the different structures of these products were readily revealed by the $\nu(CO)$ regions of their infrared spectra. This difference in behavior of the analogous molybdenum and tungsten anions can be attributed to the lower strengths of molybdenum—carbon bonds relative to corresponding tungsten—carbon bonds [26] which allows the rupture of the metal—alkyl bond necessary for formation of the cyclic acyl derivative XVII to occur only in the case of the molybdenum derivative.



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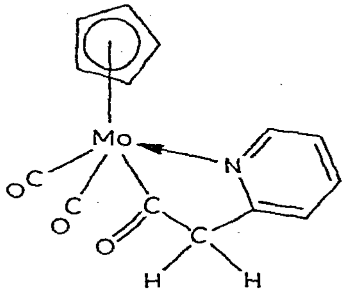

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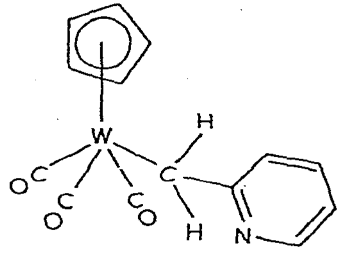
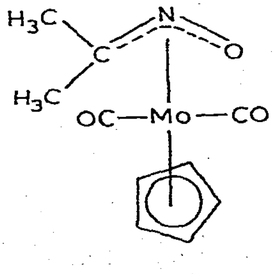
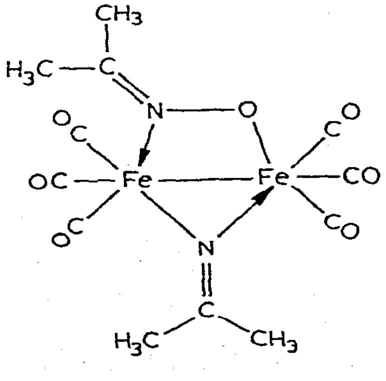


(XVIII)

Another potentially reactive group towards transition metal systems is the *C*-nitroso group. We recently investigated some reactions of the nitrosoalkyl halide $(CH_3)_2C(NO)Br$ with metal carbonyl anions [27]. Treatment of $(CH_3)_2C(NO)Br$ with $NaMo(CO)_3C_5H_5$ gave purple crystalline $(CH_3)_2C(NO)Mo(CO)_2C_5H_5$, shown by X-ray crystallography [28] to have structure XIX with the carbon, nitrogen, and oxygen of the $(CH_3)_2CNO$ group bonded to the metal atom. Other reactions of $(CH_3)_2C(NO)Br$ with metal carbonyl anions resulted in reduction of the nitroso group to an imino group to give metal derivatives of dimethylketimine such as $(CH_3)_2C{=}N(H)M(CO)_5$ (M = Cr and W) and $[(CH_3)_2C{=}NFe(CO)_3]_2$ from $Na_2M_2(CO)_{10}$ (M = Cr and W) and $Na_2Fe(CO)_4$, respectively. A still more unusual product from the reaction of $(CH_3)_2C(NO)Br$



(XIX)



(XX)

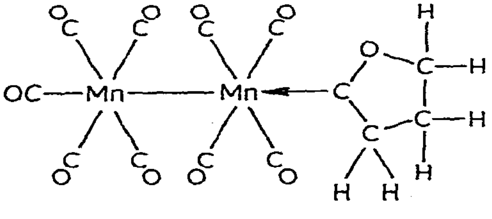
with $Na_2Fe(CO)_4$ was $[(CH_3)_2C{=}N]_2OFe_2(CO)_6$. Our postulated [27] structure XX for this last complex has been recently confirmed by X-ray crystallography [28].

Another problem which first arose during my graduate school period at Harvard was the synthesis of perfluoroaryl-transition metal derivatives. Actual work on this problem, however, had to await the availability of the necessary polyfluoro-aromatic compounds which first became available to me in 1963 during my period at the Mellon Institute. Our successful approach to polyfluoroaryl transition metal derivatives was suggested by the reported [29] nucleophilic substitution of polyfluoro-aromatic compounds with reagents such as methoxide to give the corresponding polyfluoroaryl derivatives with elimination of fluoride ion. We felt that transition metal carbonyl anions might be sufficiently nucleophilic to displace fluoride from a polyfluoro-aromatic compound to give polyfluoroaryl-transition metal derivatives. These expectations were fulfilled when we found that hexafluorobenzene reacted with $NaFe(CO)_2C_5H_5$ to form a relatively good yield of the pentafluorophenyl derivative $C_6F_5Fe(CO)_2C_5H_5$ [30]. Similar polyfluoroaryliron derivatives were analogously obtained from reactions of $NaFe(CO)_2C_5H_5$ with other polyfluoroarenes such as pentafluorobenzene and octafluorotoluene. The research group of Stone [31] and Rausch [32] independently prepared at about the same time several pentafluorophenyl-transition metal derivatives by a different approach using reactions of pentafluorophenyllithium and pentafluorophenylmagnesium bromide, respectively, with various transition metal halides. Our approach to polyfluoroaryl-transition metal derivatives from nucleophilic substitution of fluorine atoms in polyfluoro-aromatic compounds bonded to sp^2 carbons with metal carbonyl anions has subsequently been developed extensively in the laboratory of my former thesis adviser at Harvard, Professor F.G.A. Stone, now for many years at the University of Bristol in England, and has been shown to introduce a wide variety of polyfluoro-aromatic, polyfluoro-heterocyclic, and polyfluorovinylic groups into transition metal systems, particlarly $C_5H_5Fe(CO)_2$ derivatives [33].

Our success in the preparation of $C_6F_5Fe(CO)_2C_5H_5$ from hexafluorobenzene and $NaFe(CO)_2C_5H_5$ led to an investigation of the analogous reactions of hexafluorobenzene with the related metal carbonyl anions $NaM(CO)_3C_5H_5$ (M = Mo and W), $NaMn(CO)_5$, and $NaCo(CO)_4$ in attempts to prepare pentafluorophenyl derivatives of these metals. These attempts were uniformly unsuccessful [30]. This suggested that the anion $C_5H_5Fe(CO)_2^-$ was much more nucleophilic than the other anions tried thereby making of interest an investigation of the relative nucleophilicities of different metal carbonyl anions. Fortunately, at that time I was involved in a collaborative project with Professor Dessy on the electrochemistry of the numerous transition metal organometallic derivatives which had become available from the synthetic studies in my laboratory [34, 35]. This electrochemical work suggested that the concentration of metal carbonyl anions in solution could be monitored by polarographic techniques and made feasible a relative rate study of reactions of different metal carbonyl anions with the same alkyl halides. We therefore investigated the relative rates of reactions of the various metal carbonyl anions with various alkyl halides. This allowed us to establish the following series of relative nucleophilicities of the metal carbonyl anions used in this work [36]: $C_5H_5Fe(CO)_2^-$ (70,000,000) > $C_5H_5W(CO)_3^-$

(~500) > $Mn(CO)_5^-$ (77) ≈ $C_5H_5Mo(CO)_3^-$ (67) > $Co(CO)_4^-$ (1). The extremely high nucleophilicity of $C_5H_5Fe(CO)_2^-$ relative to the other four anions listed above accounts for its unique ability among these five anions to displace fluoride from hexafluorobenzene [30]. The anions $C_5H_5Ru(CO)_2^-$ and $Re(CO)_5^-$ also were found to have relatively high nucleophilicities (7,500,000 and 25,000, respectively) and later [37, 38] were shown by Stone and coworkers to react with polyfluoroarenes analogously to $C_5H_5Fe(CO)_2^-$ to form the corresponding polyfluoroaryl-transition metal derivatives.

The widely differing nucleophilicities of different metal carbonyl anions also account for many other aspects of their chemistry. For example, the extremely nucleophilic $NaFe(CO)_2C_5H_5$ reacts with the α,ω-dibromoalkanes $Br(CH_2)_nBr$ ($n = 3$ and 4) with replacement of both bromines [39] to give the diiron derivative $C_5H_5Fe(CO)_2(CH_2)_nFe(CO)_2C_5H_5$ whereas the much less nucleophilic $NaMo(CO)_3C_5H_5$ reacts with the same α,ω-dibromoalkanes under the same conditions with replacement of only one bromine [40] to give the bromoalkyl derivative $Br(CH_2)_nMo(CO)_3C_5H_5$. Furthermore, these bromoalkylmolybdenum derivatives react with $NaFe(CO)_2C_5H_5$ with elimination not only of bromide but also of the less nucleophilic $C_5H_5Mo(CO)_3^-$ to give the same diiron derivatives $C_5H_5Fe(CO)_2(CH_2)_nFe(CO)_2C_5H_5$ obtained directly from the α,ω-dibromoalkanes and $NaFe(CO)_2C_5H_5$. An apparent anomaly is the replacement of both bromines in $Br(CH_2)_3Br$ by $NaMn(CO)_5$, of comparable nucleophilicity to $NaMo(CO)_3C_5H_5$, to give a compound of the stoichiometry $(CH_2)_3Mn_2(CO)_{10}$ [41]. However, our original spectroscopic data, reported in 1963, indicated that this manganese compound could not be the simple $(OC)_5MnCH_2CH_2CH_2Mn(CO)_5$ analogous to the iron complex mentioned above. The correct structure for this manganese compound as a cyclic carbene metal complex XXI was deduced by Casey only in 1970 in a very elegant piece of work [42]. If anyone had been clairvoyant and imaginative enough to postulate this correct structure XXI for $(CH_2)_3Mn_2(CO)_{10}$ back in 1963, I do not think that he would have been believed since at that time there was no established precedent for metal—carbene complexes. Fischer and Maasböl [43] identified the first stable metal—carbene complexes only in 1964 and further work [44] extending over a period of years was necessary before the basic features of the chemistry of this class of metal complexes was understood.



(XXI)

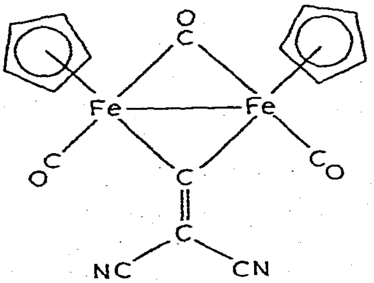
My work with metal carbonyl anions while at the Mellon Institute also provided the first synthesis of arylazo-transition metal derivatives in 1964 [45, 46]. The analogy between metal carbonyls and nitrosyls suggested that arylazo ligands, RNN, might form metal complexes similar to the aryl (and alkyl) isocyanides, RNC. The obvious method for the preparation of arylazo transition metal derivatives appeared to be the reaction of aryldiazonium tetrafluoroborates with appropriate metal carbonyl anions. However, our attempts to prepare $C_6H_5NNMo(CO)_2C_5H_5$ from benzenediazonium tetrafluoroborate and $NaMo(CO)_3C_5H_5$ were unsuccessful unit the day that my research assistant, Mr. Milton Bisnette, miscalculated the stoichiometry and used only half of the calculated amount of *p*-anisyldiazonium tetrafluoroborate in a reaction with $NaMo(CO)_3C_5H_5$. This miscalculated reaction gave the first arylazo-transition metal complex *p*-$CH_3OC_6H_4NNMo(CO)_2C_5H_5$. Further work [46] indicated that arylazo derivatives of the type $RNNMo(CO)_2C_5H_5$ were readily decomposed by electrophilic reagents, including aryldiazonium ions. This made it necessary to carry out the reaction between the aryldiazonium tetrafluoroborate and $NaMo(CO)_3C_5H_5$ either by mixing the reagents at —78° and warming to room temperature only at a later stage or by using excess $NaMo(CO)_3C_5H_5$ as had been done inadvertently in the original successful experiment cited above.

An interesting reaction reported towards the end of my period at the Mellon Institute was the observation by Wannagat and Seyffert [47] that sodium bis(trimethylsilyl)amide could replace the oxygen of a carbonyl group in the metal carbonyls $Ni(CO)_4$ and $Fe(CO)_5$ by a nitrogen atom to give the corresponding cyanocarbonylmetallates $Ni(CO)_3CN^-$ and $Fe(CO)_4CN^-$. We felt that the octahedral metal carbonyls, $M(CO)_6$ (M = Cr, Mo, and W) might give more stable derivatives of this type and therefore investigated their reactions with sodium bis(trimethylsilyl)amide [48]. This provided a facile synthesis of the pure sodium salts $NaM(CO)_5CN$, which, unlike sodium salts of the other metal carbonyl anions discussed in this paper, were apparently stable to air oxidation. The nucleophilicities of the anions $M(CO)_5CN^-$ (M = Cr, Mo, and W) were too low [36] for them to be alkylated with the usual alkyl halides. Furthermore, reactions of $M(CO)_5CN^-$ with more reactive electrophiles occurred at the nitrogen rather than the metal. Thus, the treatment of an aqueous solution of the $NaM(CO)_5CN$ (M = Cr, Mo, and W) salts with hydrochloric acid gave the white volatile crystalline $HNCM(CO)_5$ (M = Cr, Mo, and W), of significance in being the first stable metal carbonyl complexes with a hydrogen isocyanide ligand. The synthesis of hydrogen isocyanide complexes by protonation of appropriate metal carbonyl cyanide anions has subsequently been extended to other systems including $C_5H_5Mn(CO)_2(CNH)$ [49].

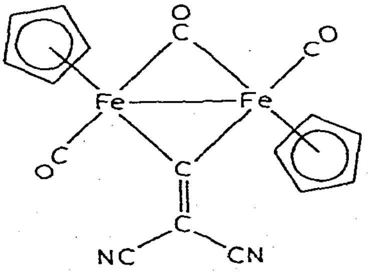
Some recent studies on the reactions of unusually reactive vinylic halides with metal carbonyl anions have resulted in the discovery of unusual and exciting new organometallic compounds. The simple vinyl halides $CH_2{=}CHX$ are well known to be very unreactive towards nucleophilic substitution. Thus even the extremely nucleophilic $NaFe(CO)_2C_5H_5$ reacts with vinyl chloride to give only a ~2% yield of $CH_2{=}CHFe(CO)_2C_5H_5$ [50]. However, introduction of appropriate substituents onto the olefinic carbons of the vinyl halides can make them as reactive as acyl chlorides towards nucleophiles. Such activated vinyl halides should react with metal carbonyl anions to form extensive series of vinyl transition metal derivatives.

The first studies on reactions of activated vinyl halides with metal carbonyl anions were initiated in 1971 with the polycyanovinyl chlorides. In 1970 we started a research program on cyanocarbon chemistry. A major objective of this research program was the preparation of dicyanomethylene analogues of stable oxygen compounds. In view of our long standing interest in metal carbonyl chemistry, a cyanocarbon derivative of particular interest to us was dicyanovinylidene, $C{=}C(CN)_2$, the dicyanomethylene analogue of carbon monoxide. During the course of attempts to prepare free dicyanovinylidene we investigated both the dehydrohalogenation of $(NC)_2C{=}C(H)Cl$ and the dehalogenation of $(NC)_2C{=}CCl_2$. These reactions failed to give any conclusive evidence for the formation of the desired dicyanovinylidene. However, the experience thus gained with these polycyanovinyl chlorides made us aware of their unusually high reactivity towards nucleophiles [51] and suggested that reactions of polycyanovinyl chlorides with metal carbonyl anions might provide facile routes to novel polycyanovinyl transition metal derivatives. In accord with this expectation, reactions of the polycyanovinyl halides $(NC)_2C{=}C(X)Cl$ ($X = H$, Cl and CN) with the metal carbonyl anions $C_5H_5M(CO)_3^-$ ($M =$ Mo and W) and $Mn(CO)_5^-$ were found to give good yields of the polycyanovinyl transition metal derivatives $(NC)_2C{=}C(X)M(CO)_3C_5H_5$ ($X = H$, Cl, and CN; $M =$ Mo and W) and $(NC)_2C{=}C(X)Mn(CO)_5$ ($X = H$, Cl, and CN), respectively [52, 53].

This study on the reactions of polycyanovinyl chlorides with metal carbonyl anions also resulted in the preparation of the first transition metal dicyanovinylidene derivative, albeit by accident rather than design. Whereas the reaction of $(NC)_2C{=}CCl_2$ with $NaMo(CO)_3C_5H_5$ resulted in the replacement of one chlorine atom with the transition metal moiety to give $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ as discussed above, the corresponding reaction of $(NC)_2C{=}CCl_2$ with the much more nucleophilic $NaFe(CO)_2C_5H_5$ resulted in the replacement of both chlorine atoms to give two isomers XXIIa and XXIIb of the complex $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ containing a bridging dicyanovinylidene ligand. These two isomers did not interconvert readily in contrast to the corresponding isomers of the carbonyl derivative $[C_5H_5Fe(CO)_2]_2$ suggesting fundamentally different properties of the carbonyl and dicyanovinylidene ligands [54]. The high carbonyl $\nu(CO)$ frequencies in $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ relative to the corresponding carbonyl $\nu(CO)$ frequencies in the carbonyl $[C_5H_5Fe(CO)_2]_2$ suggested that the dicyanovinylidene ligand is a stronger π-acceptor than carbon monoxide, normally regarded as one of the strongest π-acceptors in transition metal chemistry.

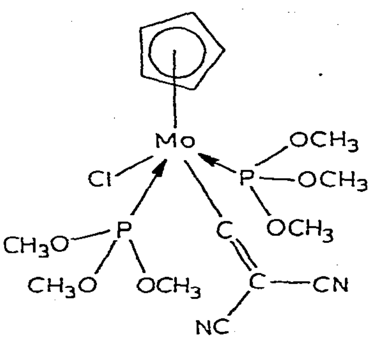


(XXIIa)

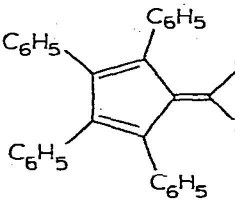


(XXIIb)

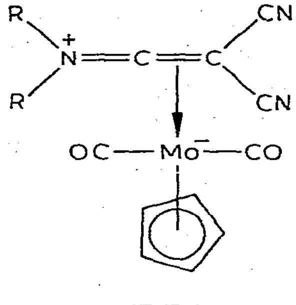
The reactions of the molybdenum complex $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with various nucleophiles were investigated in attempts to replace the remaining chlorine atom with other reagents. Triphenylphosphine reacted with this molybdenum complex under surprisingly mild conditions with complete replacement of all three carbonyl groups with two triphenylphosphine ligands to give an orange product formulated as the terminal dicyanovinylidene complex $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ largely from proton NMR evidence indicating the two stereoisomers expected for a $C_5H_5MA_2BC$ derivative rather than only the single isomer expected for a $C_5H_5MA_2B$ derivative [55, 56]. The proposed formulation of this molybdenum derivative as a terminal dicyanovinylidene complex was later confirmed by carbon-13 NMR [57] and X-ray crystallographic [58, 59] data on the related trimethyl phosphite derivative $C_5H_5Mo[P(OCH_3)_3]_2[C{=}C(CN)_2]Cl$ (XXIII).



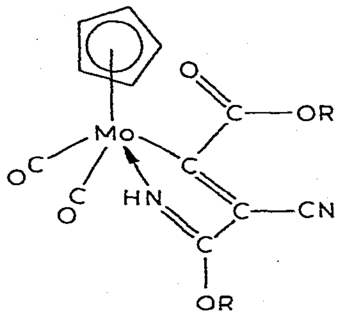
(XXIII)



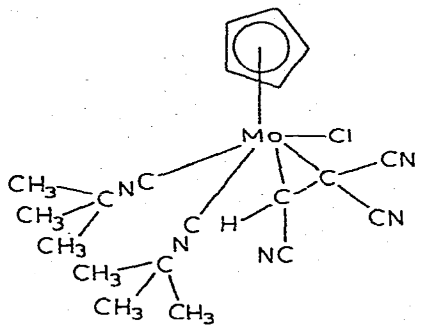
(XXIV)



(XXV)



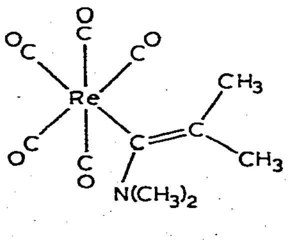
(XXVI)



(XXVII)

Other reactions of the 1-chloro-2,2-dicyanovinylmolybdenum complex $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ make this compound one of the most bizarre compounds encountered during my sixteen years in transition metal organometallic chemistry. This molybdenum complex acts as a source of dicyanovinylidene in its reaction with diphenylacetylene to give the olive green 6,6-dicyano-1,2,3,4-tetraphenylfulvene (XXIV), a dicyanomethylene analog of tetraphenylcyclopentadienone [60]. Reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with secondary amines such as dimethylamine and piperidine give the yellow dicyanoketeneimmonium derivatives $[R_2N{=}C{=}C(CN)_2]Mo(CO)_2C_5H_5$ (XXV). Other basic reagents, e.g. sodium methoxide, form novel chelates (XXVI: $R = CH_3$ or C_2H_5) with $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ [61]. Finally, t-butyl isocyanide reacts with $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with apparent elimination of isobutylene to form two stereoisomers of the tricyanoethylene derivative $C_5H_5Mo[CNC(CH_3)_3]_2$-$[(NC)_2C{=}CHCN]Cl$, e.g. XXVII [62].

An even more interesting activated vinyl halide for forming unusual organometallic derivatives with metal carbonyl anions is the 1-aminovinyl halide $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ [63, 64]. Indeed, this is probably the most versatile single reagent for reactions with metal carbonyl anions since the $(CH_3)_2C{=}C$-$[N(CH_3)_2]$ unit from the halide can bond to transition metals in no less than six different ways in various products obtained from such reactions. The structures of the resulting products can be elucidated unambiguously with the help of proton and carbon-13 NMR spectroscopy to determine the equivalence or non-equivalence of both the *C*-methyl and *N*-methyl groups of the $(CH_3)_2C{=}C$-$[N(CH_3)_2]$ unit. The reaction of $NaRe(CO)_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ at room temperature gives a mixture of the *monohapto*-vinyl derivative XXVIII and what we call the *C,C-dihapto*-cyclic acyl derivative XXIX. Mild heating of XXIX causes its smooth conversion to XXVIII. However, reaction of the analogous manganese anion salt $NaMn(CO)_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ follows a completely different course, since the initial product isolated is the yellow *C,N-dihapto*-cyclic acyl derivative XXX. Ultraviolet irradiation or mild heating of XXX results in the facile elimination of two carbonyl groups with hydrogen migration to give the yellow 2-azabutadiene derivative XXXI. However, decarbonylation of XXX with $Fe_2(CO)_9$ (an effective, but highly unusual, decarbonylating reagent) results in the elimination of only one carbonyl group to give the yellow liquid *C,N-dihapto*-keteneimmonium derivative XXXII. A similar yellow crystalline *C,N-dihapto*-keteneimmonium derivative XXXIII is prepared from $NaMo(CO)_3C_5H_5$ and $(CH_3)_2C{=}C[N(CH_3)_2]Cl$. Protonation of XXXIII with strong acid (e.g. HPF_6) gives the 1-azaallyl derivative XXXIV which upon deprotonation with aqueous ammonia gives the relatively unstable yellow *C,C-dihapto*-keteneimmonium derivative XXXV. In its reaction with metal carbonyl anions, the halide $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ thus combines many of the features of the haloalkylamines such as $(CH_3)_2NCH_2CH_2Cl$ and the haloalkyl sulfide CH_3SCH_2Cl discussed above but also introduces many novel features of its own such as the isomerism in the *C,C*- and *C,N-dihapto*-keteneimmonium and -cyclic acyl derivatives and the hydrogen migration to form the 2-azabutadiene derivative XXXI. We feel that further investigation of the unusual products obtained from 1-aminovinyl halides and metal carbonyl anions is the most exciting area in metal carbonyl anion chemistry currently under investigation in our laboratory.



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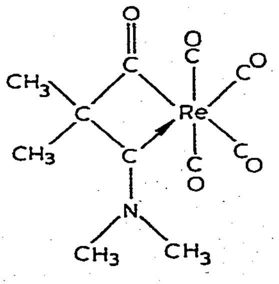

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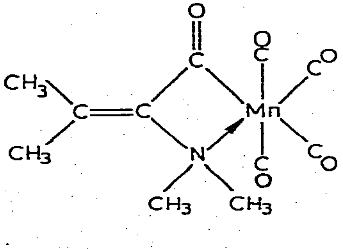

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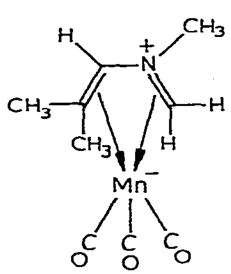
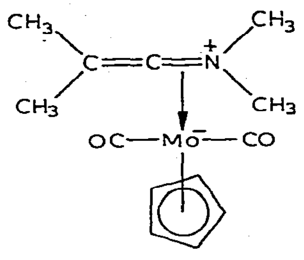

(XXXI)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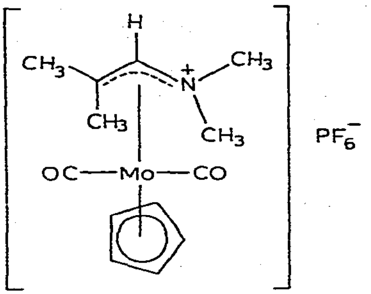
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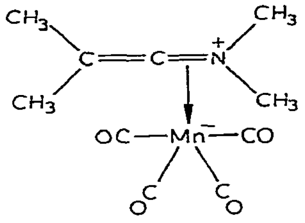
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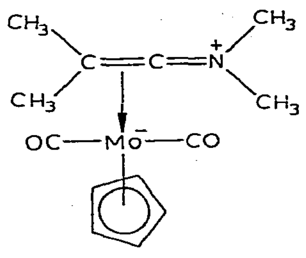
(XXXV)

In this article I have attempted to show some of the unusual and significant types of transition metal organometallic compounds which have resulted from the studies in my laboratory on metal carbonyl anions as preparative reagents. Thus the work on the *trihapto*-benzyl derivative VIII was of considerable importance in understanding fluxional organometallic molecules by providing the first system on which proton NMR spectra could be observed of both the "fixed" structure and completely equilibrating structures. Metal carbonyl anions were necessary for the preparation of numerous important and unique cyanocarbon transition metal derivatives including both polycyanovinyl and dicyanovinylidene derivatives. The first arylazo-transition metal complexes were products from metal carbonyl anion reactions. Metal carbonyl anion chemistry is often the route of choice to cyclic acyl derivatives (e.g. XIII, XV, and XVI) and to $C_5H_5Mo(CO)_2T$ derivatives where T is a novel three-electron donor ligand such as *dihapto*-CH_3SCH_2, $(CH_3)_2CNO$, and various keteneimmonium ligands (e.g. V, XIX, XXV, XXXIII, and XXXV). Our successes in metal carbonyl anion chemistry outlined in this article suggest that further investigation of this fertile field of research will continue to produce new and interesting compounds of importance in the development of many areas of chemistry.

Acknowledgement

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