ARYLDIAZENIDO AND DINITROGEN COMPLEXES OF MANGANESE

by

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ABSTRACT

Aryldiazenido complexes of manganese, $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4R)][BF_4]$ (R = CF_3, F, H) have been prepared by reacting aryldiazonium tetrafluoroborate salts with $[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2Si(C_6H_5)_3]$ in acetone at room temperature. These complexes react with a variety of nucleophilic agents X^- (X^- = Cl^-, Br^-, I^-, CN^-, SCN^-), to give the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$, being the first example of synthesis of a dinitrogen complex by using an aryldiazenido compound as an intermediate. Reactions of other related aryldiazenido complexes: $[M(CO)_2(PPh_3)_2(N_2R)][BF_4]$(M = Fe, Ru), $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(N_2R)]$, $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2R)][BF_4]$ (R = $\underline{o}\text{-}C_6H_4CF_3$); with these nucleophilic agents were carried out, in order to determine if this reaction is typical for singly bent aryldiazenido compounds.

Manganese-aryldiazenido complexes reacted with triphenylphosphine to give, initially, the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn\ (CO)_2N_2]$ as an intermediate which was consumed during the reaction to give finally the known mono-substituted triphenylphosphine derivative $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$.

The structure of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ has been determined by x-ray crystallography. This compound crystallizes from acetone diethyl ether as solvent-free crystals in space group C_{2v}^{19} - F_{dd2} of the orthorhombic system with $\underline{a}$ = 12.866(3) Å, $\underline{b}$ = 56.605(11) Å, $\underline{c}$ = 9.964(2) Å, $\alpha = \beta = \gamma = 90°$ and Z = 16. Based upon 1019 unique reflections with $I > 2.3\ \sigma_I$

the structure was solved and refined by full-matrix, least-squares methods, to $R = 0.053$ and $R_w = 0.055$. The aryldiazenido ligand in the compound has the singly-bent geometry, in agreement with that deduced previously from the ν (NN) frequency; Mn-N-N = 171.8(8)°, N-N-C = 125.6(9)°, N-N = 1.211(8) Å.

To Magaly, Ana Maria and Paola

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CHAPTER I

ARYLDIAZENIDO AND DINITROGEN COMPLEXES OF MANGANESE

INTRODUCTION:

The study of transition-metal complexes containing aryldiazo ligands (ArNN), as well as other ligands which contain nitrogen-nitrogen multiple bonds, has been of great interest because of their close relationship to nitrosyl and dinitrogen ligands and also because of their varied modes of bonding and their utility as intermediates in the synthesis of aryldiazene and arylhydrazine ligands.[1,2,3]

Diazonium ions can be described as (1) and they react normally as electrophiles through the terminal nitrogen atom. They have yielded numerous stable complexes with transition-metal derivatives.

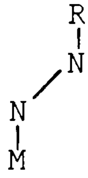
$$R-\overset{+}{N}\equiv N:$$

(1)

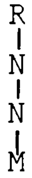
1.1 STRUCTURE OF ARYLDIAZO LIGANDS

There are several attainable coordination geometries for aryldiazo ligands with transition metals, and they are indicative of their chemical versatility.[1-4]

(A)



(B)



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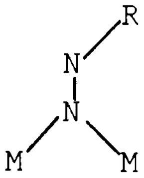

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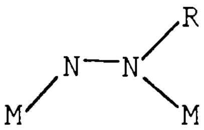


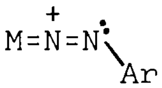
(E)

Structural studies have shown that the aryldiazo ligands can adopt a singly-bent geometry (A), doubly-bent geometry (B) and can bridge two metal atoms (D).

The bonding modes totally linear geometry (C) and double-nitrogen bridged geometry (E) remain unobserved.

In the <u>singly-bent case</u> (A), the aryldiazo ligand may be viewed as a three-electron donor terminal ligand and the bonding is described as σ-donation from a sp hybrid orbital on the terminal nitrogen atom with strong π-back donation from d-orbitals on the metal into a p-orbital on the terminal nitrogen.

A simple valence bond description of this type of complex is (2), where a N-N-Ar angle of 120° is expected.



$$M{=}\overset{+}{N}{=}\ddot{N}{-}Ar$$

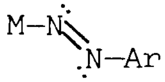
(2)

This bonding mode is the more common and has been observed in the complexes: $[(HBpz_3)Mo(CO)_2(N_2C_6H_5)]^5$, $[Fe(CO)_2(PPh_3)_2(N_2C_6H_5)][BF_4]^6$, $[OsH(CO)(PPh_3)_2(N_2C_6H_5)]^7$,

$[ReCl_2(PPhMe_2)_3(N_2C_6H_5)]^8$, $[Mo(S_2CNMe_2)_3(\underline{m}\text{-}N_2C_6H_4R)]^9$ (R = H, NO_2); $[RuCl_3(PPh_3)_2(\underline{p}\text{-}N_2C_6H_4Me)]^{36,51}$, $[ReCl_2(PMe_2Ph)_3(N_2COPh)]^{61}$.

The experimental value for the N-N-Ar angle, close to 120° in these complexes, suggests the importance of back-bonding in this type of geometry (see Table 9).

In the <u>doubly-bent</u> terminal structure (B), the aryldiazo ligand can be viewed as a one-electron donor (ArN_2) radical or as a two-electron donor (ArN_2^-) ligand, where the bonding is described as the overlap between a sp^2 orbital on the terminal nitrogen atom with a hybrid orbital on the metal (3).



(3)

With an ArN_2^- ligand, the aryldiazenido complexes should possess an angle of 120° at both nitrogen atoms and the metal suffers a formal two-electron oxidation, when this arises by bonding to the ArN_2^+ ion.

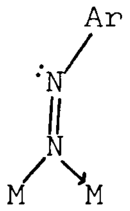
This type of structure has been observed by x-ray crystallography in very few cases. Three of them are: $[PtCl(PEt_3)_2(\underline{o}\text{-}N_2C_6H_4F)]^{10}$, $[IrCl_2(CO)(PPh_3)_2(\underline{o}\text{-}N_2C_6H_4NO_2)]^{11}$ and $[RhLCl(N_2C_6H_5)][(PF_6]^{62}$ $L = C_6H_5P\{(CH_2)_3P(C_6H_5)_2\}_2$.

There are many other complexes which are believed to contain the ArN_2^- ligand, supported by IR, NMR spectroscopy or site of protonation. In complexes with doubly-bent geometry, protonation at N^1, the nitrogen atom adjacent to the metal, is expected.[1] The complex $[RhCl_2(PPh_3)_2(N_2C_6H_5)]$ is protonated with HCl in Et_3N at N^1 to give $[RhCl_3(PPh_3)_2(NH{=}NC_6H_5)]$[63].

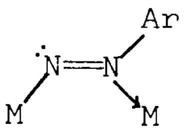
The N-N distances in the above structures are 1.17(3), 1.19(4) and 1.172(9) Å respectively. The last value is in between that expected for a double and triple nitrogen-nitrogen bond. The first two values have large standard deviations, being not significantly different from the accepted value of a N-N double bond. (1.24 Å, from PhN_2Ph)[12,13]. The accepted value for a N-N triple bond is 1.10 Å (from the free ligand PhN_2^+)[14]. The angles M-N-N are 118(2), 115(3) and 125.1(6)° respectively. These experimental results are in agreement with the "doubly-bent" formalism.

<u>Bridging ArN_2:</u>

The aryldiazo ligand may, in principle, bridge two metal atoms in single-nitrogen (4) or double-nitrogen (5) bridged structures.



(4)



(5)

In both cases, the ligand supplies three-electrons to the system.

The bridged structure has been observed in only three transition-metal complexes and, in all of them, the structure observed is single-nitrogen bridged geometry: $[Mn(CO)_4(N_2C_6H_5)]_2$[15]; $[Ir_2O(\underline{o}\text{-}N_2C_6H_4NO_2)(NO_2)(PPh_3)_2]^{\oplus}$[16] and $[Pd_2(dppm)_2(N_2R)Cl_2][BF_4]$[17*].

In the Mn and Ir complexes, the distances M^1-N and M^2-N are almost identical and are similar in length to the M-N distances for complexes with one-electron donor aryldiazo ligands. The three electrons, donated by the aryldiazo ligand, in these bridged structures are shared equally between the two metal atoms. The distances N-N are 1.234(3) and 1.22(6) Å respectively, indicating nitrogen-nitrogen double bonds.

1.2 DIAZOCHEMISTRY OF MANGANESE

The diazochemistry of this first-row transition metal is confined to a few examples of aryldiazenido complexes and some other organometallic compounds with diazo ligands, generally with unusual coordination geometry. $MnH(CO)_3(PPh_3)_2$ reacts with benzenediazonium salts to give (after deprotonation and decarbonylation with base) a neutral aryldiazenido complex: $[Mn(CO)_2(PPh_3)_2(N_2C_6H_5)]$[18]. This complex undergoes successive carbonyl displacement in the presence of arenediazonium and halide ions to yield a series of bis-aryldiazenido complexes

---

[*] R = ortho-$CF_3C_6H_4$ or para-$CF_3C_6H_4$

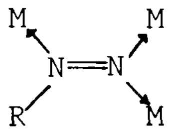
of the type : $[Mn(CO)(PPh_3)_2(N_2C_6H_5)_2]^+$ and $[MnX(PPh_3)_2(N_2C_6H_5)_2]$ (X = Cl or Br).

These complexes are expected to have terminal singly-bent aryldiazenido structures.[18]

$[Mn(CO)_4(N_2C_6H_5)]_2$[15], containing bridging N_2Ph ligands, is the only other example of an aryldiazenido compound of manganese, prior to the present study, a rare example of an unsubstituted metal carbonyl aryldiazenido complex. Reaction with triphenylphosphine produces bridge fission, giving the mononuclear five-coordinate product $[Mn(CO)_2(PPh_3)_2(N_2C_6H_5)]$, mentioned above, with the aryldiazo ligand presumed to be bonded in a singly-bent manner.

Manganese complexes containing diazo ligands other than aryldiazo ligands also are known. $RC_5H_4Mn(CO)_2THF$ reacts with $N_2C(COOC_2H_5)_2$ to give $[Mn(RC_5H_4)(CO)_2\{N_2C(COOC_2H_5)_2\}]$ (R = H or CH_3)[19]. By i.r. spectroscopy, a totally linear MNNC geometry for this complex was assigned. The infrared spectrum showed bands at 2025, 1982 and 1951 cm^{-1}(R = H) and 2022, 1979 and 1948 cm^{-1} (R = CH_3), where the first two bands respectively were assigned to $\nu(CO)$ and the last one to $\nu(NN)$. The high value of $\nu(NN)$ was considered to indicate the presence of a N-N triple bond.

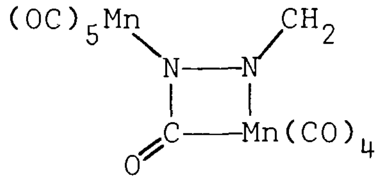
$CH_3N_2\{Mn(CO)_4\}_3$[20] is the only example where the methyl diazo ligand is triply binding (6).



(6)

The terminal nitrogen atom (acting as a three-electron donor) forms a coordination bridge between two manganese atoms and the central nitrogen atom, acting as a two-electron donor atom, is bonded to another tetracarbonyl-manganese fragment.

From the reaction of $Mn(CO)_5H$ and excess of diazomethane at low temperature, was isolated, among other products, $[Mn_2(CO)_{10}N_2CH_2]$ a binuclear complex, where the diazomethane has been introduced as an unfragmented species, bonding two $Mn(CO)_5$ moieties. The terminal nitrogen atom of the ligand is also bonded to one of the terminal carbonyl groups, converting it into an acyl function, forming an unusual four membered framework (7). This has been established by x-ray crystallography[21].



(7)

1.3 DINITROGEN COMPLEXES OF MANGANESE:

During the course of studies of the nature of metal-dinitrogen interactions, many dinitrogen complexes, showing a variety of binding modes, have been synthesized and their physical and chemical properties have been studied.

Methods of preparation of dinitrogen complexes can be divided into three broad categories:[22,23]

i) Direct reaction of N_2 with a metal complex, frequently under strongly reducing conditions or replacement of labile ligands in the complex by dinitrogen (normally under high pressure of N_2).

ii) Generation in situ of the dinitrogen ligand by conversion of a ligand with an N-N bond into N_2.

iii) Metathesis of dinitrogen complexes to give new ones.

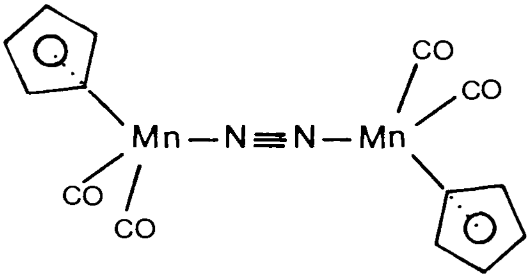
For manganese, three dinitrogen complexes are known: $[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2]$ and $[\{(\eta^5\text{-}RC_5H_4)Mn(CO)_2\}_2(N_2)]$ (R = H or CH_3). The first was synthesized by two different routes: by replacement of a labile ligand (THF) by dinitrogen under high pressure (8)[24], and by oxidation of a hydrazine ligand (9)[25].

$$[(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)] \xrightarrow[\text{THF}]{N_2\text{, 150 atm.}} [(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2)] + THF \quad (8)$$

$$[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2H_4] + 2H_2O_2 \xrightarrow[\text{THF/-40°C}]{Cu^{+2}\text{/1h}} [(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2)] + 4H_2O \quad (9)$$

By infrared and NMR spectroscopy a terminal "end-on" N_2 coordination has been assigned to this complex, and has been confirmed by x-ray photoelectron (ESCA) spectroscopy.[26] The ESCA spectrum showed a doublet structure for the N1s electrons, a direct indication of terminal bonding of the N_2 molecule to the manganese atom in an "end-on" fashion.

The $[(\eta^5\text{-RC}_5H_4)Mn(CO)_2]_2N_2$[64] complexes (R = CH_3, H) were prepared by the reaction of the THF derivative: $[(\eta^5\text{-RC}_5H_4)Mn(CO)_2THF]$ with 1,1,1-trifluorodiazoethane at -80° C in THF. The x-ray structure analysis showed the N_2 to be bound to the two manganese atoms in an "end-on bridged" structure, with the two cyclopentadienyl rings being trans to each other (10).



(10)

In this thesis will be reported the first example of the synthesis of a dinitrogen complex, namely $[(\eta^5\text{-CH}_3C_5H_4)Mn(CO)_2N_2]$ by using an aryldiazenido compound as an intermediate. The aryldiazenido complexes $[(\eta^5\text{-CH}_3C_5H_4)Mn(CO)_2(\underline{o}\text{-N}_2C_6H_4R)][BF_4]$ (R = CF_3, F, H) undergo nucleophilic attack at the carbon atom bonded to the nitrogen atom in the aryldiazo ligand to give $\underline{o}\text{-IC}_6H_4CF_3$ and leaving the N_2 fragment bonded to the metal atom to produce the dinitrogen complex $[(\eta^5\text{-CH}_3C_5H_4)Mn(CO)_2N_2]$. A parallel reaction, under an argon rather than nitrogen atmosphere, gave identical products, showing that the N_2 ligand originated in the aryldiazo group.

1.4 OBJECTIVES OF THE RESEARCH

A continuing theme in the research being carried out in our laboratory has been to gain knowledge of the metal-N_2R bonding and chemistry with a view to: a.) utilization and conversion of atmospheric N_2 into organic derivatives using transition metal intermediates; b.) understanding the factors which govern the structure and stereochemistry and properties of organodiazo groups attached to transition-metals.

The diazo chemistry of the 3d metals, especially manganese, is very limited, by comparison with 4d and 5d transition metals. We wanted to attempt to enlarge it and compare it with Cr, Fe or other analogues where possible. In particular, other workers had shown that manganese is capable of forming diazo-compounds even in the presence of solely CO groups, which is unusual.[15] It was also of interest to obtain more information about the spectroscopic properties of 3d metal aryldiazenido complexes so as to compare with those of the heavier 4d and 5d metals. For example, the ν(NN) frequencies of comparable complexes are lower for the heavier metals, indicating that they are better electron donors than the lighter ones: $[RuBr_3(PPh_3)_2(\underline{p}\text{-}N_2C_6H_4CH_3)]$, ν(NN) ▫ 1895 cm^{-1}, may be compared with $[OsBr_3(PPh_3)_2(\underline{p}\text{-}N_2C_6H_4CH_3)]$, ν(NN) = 1855 cm^{-1}.[63] (For more examples, see Table 13). However, due to the relatively few 3d metal aryldiazenido complexes, it has not been possible to obtain a complete picture of these trends for more than a few examples.

The study of this relatively light metal was also motivated by the possibility of carrying out x-ray studies on its aryldiazenido complexes, because the presence of a light metal is an advantage in permitting, in principle, a relatively accurate determination of the interesting non-metal atomic positions, especially of the aryldiazo group.

The complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ was chosen as a starting material because it was readily available and cheap, and it is an example of an arene-metal carbonyl. Possible aryldiazo complexes resulting could be compared with dinitrogen analogues. There are not many metal-dinitrogen complexes that have related aryldiazenido analogues.

As will be evident later, one of the derivatives of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ used in the syntheses was $[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3]$. This had the added interest that it allowed us to compare the previous studies on the insertion of ArN_2^+ into M-H bonds with the aryldiazo chemistry of this manganese-hydrido complex.

CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ AND OTHER RELATED ARYLDIAZENIDO COMPLEXES OF MANGANESE

2.1 SYNTHESIS:

The starting material selected was η^5-methylcyclopentadienyl tricarbonyl manganese $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$.

Substitution of the carbonyl groups in a direct reaction normally is difficult as $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ is relatively inert.

Preliminary studies of the tricarbonyl with diazonium salts showed indeed no reaction. After several experimental modifications, the starting materials were always recovered. No decomposition was noted.

Substitution of the carbonyl groups occurs under strong irradiation with ultraviolet light in the presence of a ligand with good coordination properties. Under U.V. irradiation, a carbonyl group is ejected, giving a 16-electron $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2$ intermediate,[27-29] to which the ligand readily adds. Several authors, working with $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$, have reported that the intermediate species acts as an acceptor towards many donor molecules.[29-34]

Irradiation of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ in the presence of diazonium salts cannot be performed because the ArN_2^+ ion decomposes under irradiation very quickly with N_2 gas evolution.

Three different ligands were used for the substitution of a carbonyl group under U.V. irradiation: tetrahydrofuran (THF), an olefin (cyclooctene) and triphenylsilane ($HSiPh_3$). Solutions of these complexes were then reacted with diazonium salts either in situ or after isolation and purification.

By reaction of diazonium salts with the THF derivative: $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2THF]$ in situ, no aryldiazenido complexes could be obtained. Reaction proceeded with concurrent N_2 gas evolution even at low temperatures.

The instantaneous decomposition of the diazonium salts in this reaction probably is catalyzed by secondary products produced during the photochemical reaction of the $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ in THF.

Experimental difficulties in obtaining pure, and in good yield, the cyclooctene derivative prevented the success of this method in the synthesis of aryldiazenido complexes.

Reaction of $[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3]$ with diazonium salts was, however, successful and gave several new aryldiazenido manganese complexes: $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4R)][BF_4]$ ($R = CH_3$, F, H), all of them being 18-electron systems.(11)

$$[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3] + [RC_6H_4N_2][BF_4] \xrightarrow[\text{R.T.}]{\text{acetone}}$$

$$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4R)][BF_4] + HSiPh_3 \qquad (11)$$

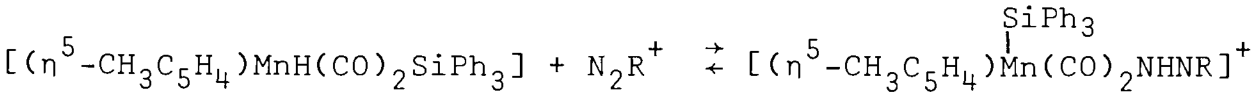
Two possible mechanisms have been considered for the substitution of $HSiPh_3$ by the aryldiazo ligands. The first envisages loss of $HSiPh_3$ first to give $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]$ as an intermediate (12). Graham and co-workers[27] produced evidence for this intermediate in the corresponding substitution of $HSiPh_3$ in $[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3]$ by PPh_3.

However, an alternative pathway not available for PPh_3, but possible for the reaction of diazonium ion, could be the insertion of the diazonium ion into the metal-hydride bond, followed by elimination of $HSiPh_3$ across the Mn-N bond (13). Insertion of diazonium ions into M-H bonds is a frequently observed reaction.[63, 67-70]

$$[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3] + L \rightleftarrows [(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2] + HSiPh_3 + L$$

$$\rightarrow [(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2L] + HSiPh_3 \qquad (12)$$

L: aryldiazo ligands.



$$[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3] + N_2R^+ \rightleftarrows [(\eta^5\text{-}CH_3C_5H_4)\overset{SiPh_3}{\overset{|}{Mn}}(CO)_2NHNR]^+$$

$$\rightarrow [(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2R]^+ + HSiPh_3 \qquad (13)$$

The infrared spectrum of the reaction mixture of the cyclooctene derivative with diazonium ions did show the formation of the corresponding aryldiazenido complex. This could therefore be taken as indication that the mechanism is via the 16-electron intermediate $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]$ and not M-H insertion, but in the absence of kinetic experiments it is not possible to go any further than this.

In all of these reactions, four different diazonium salts were tested: $[\underline{o}\text{-}RC_6H_4N_2][BF_4]$ (R = CF_3, F, H) and $[\underline{p}\text{-}CH_3OC_6H_4N_2][BF_4]$. Only the $\underline{o}\text{-}CF_3C_6H_4N_2$- and $\underline{o}\text{-}FC_6H_4N_2$-derivatives were isolated, as a deep red-violet air-stable solid and as a red-brownish air-sensitive solid, respectively.

These compounds were well characterized and a full three-dimensional single crystal x-ray structure analysis on the ortho-trifluoromethylphenyldiazenido derivative was carried out.

The non-substituted phenyldiazenido complex (R = H) was characterized in solution by i.r. spectroscopy, but could not be isolated even at low temperature. Its solutions became darker in a short period of time with the disappearance of the carbonyl bands in the i.r. spectrum.

In all reactions with $[\underline{p}\text{-}CH_3OC_6H_4N_2][BF_4]$ spectroscopic evidence of the formation of the corresponding aryldiazenido complex never could be obtained.

2.2 CHARACTERIZATION OF $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4R)][BF_4]$ (R = CF_3, F, H)

The aryldiazenido complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ crystallizes as air-stable red-violet long needles from acetone/diethyl ether solution. Its infrared spectrum showed two carbonyl stretching frequencies and one ν(NN) frequency (see Table 1).

The ν(CO) frequencies were assigned by comparison with $[Fe(CO)_2(PPh_3)_2(N_2C_6H_5)][BF_4]$[6], $[Ru(CO)_2(PPh_3)_2(N_2C_6H_5)][PF_6]$[56], $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]^+$[45] and $[(5\text{-exo}CH_3C_5H_5)Mn(CO)_2(NO)]$[52] and ν(NN) by comparison with the same iron complex.

Other characteristic infrared bands of this complex are: 1320s (CF_3 group) and 1100-1000 cm^{-1} br, vs (BF_4^- anion).

The infrared spectra of the other derivatives (R = F, H) showed the same pattern as described before (see Table 1).

No ^{15}N isotopic substitution studies have been performed in order to confirm the ν(NN) assignment, essentially because it is not practical due to the low experimental yield of the aryldiazenido complexes.

All of these spectra were taken in silver chloride cells since these complexes reacted with potassium bromide or sodium chloride windows. These reactions will be explained later (Chapter IV).

Infrared studies have been shown to be useful for examining the interaction of the aryldiazo ligand with the transition metal to which it is bonded, and the influence other ligands present in the complex. The N-N stretching vibration for a terminal aryldiazo ligand is found within the broad region ca. 1440-2200 cm^{-1}. This wide region is partly a reflection of the different possible coordination modes of the aryldiazo ligand. Generally speaking values of ν(NN)

TABLE 1

Infrared Data for $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4R)][BF_4]$ †

Compound	Solvent	ν(CO)	ν(NN)	ν'(NN)(a)
R = CF_3	$CHCl_3$:	2090 vs, 2045 vs	1795 vs	1715
	Acetone:	2083 vs, 2041 vs	1785 br, w	1705
R = F	$CHCl_3$:	2085 vs, 2042 vs	1792 vs	1712
	Acetone:	2080 vs, 2037 vs	(*)	
R = H	$CHCl_3$:	2085 vs, 2038 vs	1790 s	1710
	Acetone:	2078 vs, 2032 vs	(*)	

† Frequencies in cm^{-1}, (a) Modified values by using the empirical rules proposed by Haymore and Ibers[36]; vs, very strong; s, strong; w, weak; br, broad. (*) obscured

greater than 1650 cm^{-1} can almost certainly be attributed to a singly-bent geometry (A) and values of ν(NN) lower than 1550 cm^{-1} correspond to the doubly-bent geometry (B). With values in the intermediate region, the assignment is not trustworthy. Haymore and Ibers[36] have proposed some empirical rules which allow one to compensate for differing metal, charge and ligands, and so bring the ν(NN) values to a common scale. This to some extent then reduces the doubtful region (see Tables 1 and 2).

The complexes presently described show a strong band in the region 1800-1790 cm^{-1} which has been assigned as the N-N stretching frequency. Fortunately, in this region, resonance interaction of this stretching vibration with other ligand vibrational modes, especially weak phenyl vibrational modes, would not be expected.[35]

The high value of ν(NN) may be partly accounted for by the cationic nature of the complexes. If it is assumed that the positive charge resides mainly on the metal, this would result in a lower degree of back bonding to the diazonium group compared with the neutral compounds.[37]

The ν(NN) frequency in these complexes (1800-1790 cm^{-1}) occurs approximately 200-240 cm^{-1} higher than in the neutral complexes $[LMo(CO)_2(N_2Ar)]$ (ν(NN): 1565-1545 cm^{-1}) (L: $HBpz_3$ or C_5H_5)[38-40] and $(C_5H_5)Cr(CO)_2(\underline{p}\text{-}N_2C_6H_4X)$ (ν(NN): 1590-1570 cm^{-1}) ($X = OCH_3$, CH_3, H or F)[41]. In agreement, the carbonyl frequencies ν(CO) also occur 100-150 cm^{-1} higher than in the neutral complexes.

TABLE 2

INFRARED DATA FOR SOME SINGLY-BENT ARYLDIAZENIDO COMPLEXES†

Compound	ν(CO)	ν(NN)	ν'(NN)	Ref.
$OsH(CO)(PPh_3)_2(N_2C_6H_5)$	1911	1543	1563	7
$ReCl_2(PPhMe_2)_3(N_2C_6H_5)$		~1535	1585	8
$[Fe(CO)_2(PPh_3)_2(N_2C_6H_5)][BF_4]$	2038, 1978	1723	1593	6
$Mo(HBPz_3)(CO)_2(N_2C_6H_5)$	1994, 1904	~1590	1660	5
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$	2090, 2045	1795	1715	(a)
$RuCl_3(PPh_3)_2(\underline{p}\text{-}N_2C_6H_4CH_3)$		1881	1851	36,51
$[IrCl(PPh_3)_2(N_2C_6H_5)][PF_6]$		1868	1838	65
$[IrCl(PPh_3)_3(N_2C_6H_5)][PF_6]$		1651	1591	65
$[Ru(bipy)_2Cl(\underline{p}\text{-}N_2C_6H_4CH_3)][PF_6]_2$		2080	1910	66
$[Ru(bipy)_2Cl(\underline{p}\text{-}N_2C_6H_4OCH_3)][PF_6]_2$		2095	1925	66

† Frequencies in cm^{-1}; (a) This work.

An increase in ν(CO) implies an increase in the C-O bond order, a consequence of diminished dπ - pπ back donation by the metal.

A high value of ν(NN) also has been found in the cationic complex $[Fe(CO)_2(PPh_3)_2(N_2C_6H_5)]^+$ [37,42] (ν(NN) = 1723 cm^{-1}), up to 120 cm^{-1} higher than in the isoelectronic neutral complexes: $[Mn(CO)_2(PPh_3)_2(N_2C_6H_5)]$[18] (ν(NN) = 1612, 1543, 1476 cm^{-1}) and $[Re(CO)_2(PPh_3)_2(N_2C_6H_5)]$[18] (ν(NN) = 1605, 1538, 1471 cm^{-1}). A somewhat parallel situation in related isostructural nitrosyl complexes was reported.[37] The cationic complex $[Fe(CO)_2(PPh_3)_2(NO)]^+$ [44] shows both the ν(CO) and ν(NO) values are up to 100 cm^{-1} higher than in the isoelectronic neutral complex $[Mn(CO)_2(PPh_3)_2(NO)]$.

A similar effect also is observed in another pair of related nitrosyl complexes. The ν(CO) in the cationic $[(C_5H_5)Mn(CO)_2NO]^+$ [45,46] occurs at up to 74 cm^{-1} higher than in the neutral related nitrosyl $[(5\text{-exo}CH_3C_5H_5)Mn(CO)_2(NO)]$[47]. The ν(NO) in the cationic complex occurs at 100 cm^{-1} higher than in the neutral one.

The occurrence of ν(CO) bands in the $[(C_5H_5)Mn(CO)_2NO]^+$ complex (νCO): 2096, 2049 cm^{-1}) at higher values than in the isoelectronic also cationic complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2C_6H_5)]^+$ (ν(CO): 2090, 2045 cm^{-1}) is indicative that the nitrosyl ligand is a possibly slightly better π-acceptor than the aryldiazonium group, in agreement with other evidence reported in the literature.[2]

The C-O and N-N stretching frequencies in the complexes $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4R)][BF_4]$ (R = CF_3, F or H) were just slightly sensitive to the electron-withdrawing capacity of the ortho substituent R on the aryldiazo ligand.

Cenini and co-workers[48] found that ν(CO) values are sensitive to the electron-withdrawing capacity of the para-substituent in the $[Ru(CO)_2(PPh_3)_2(\underline{p}\text{-}N_2C_6H_4X)]^+$ complex (X = NO_2, F, OCH_3, H or $N(CH_3)_2$). The CO stretching frequencies decreased on going from X = NO_2 to X = $N(CH_3)_2$ as expected. On the other hand, Fisher and Sutton[37] found a small effect of para-substituents in the complex $[Fe(CO)_2(PPh_3)_2(\underline{p}\text{-}N_2C_6H_4X)]^+$ (X = F, Cl, Br, H, NO_2, OCH_3, OH).

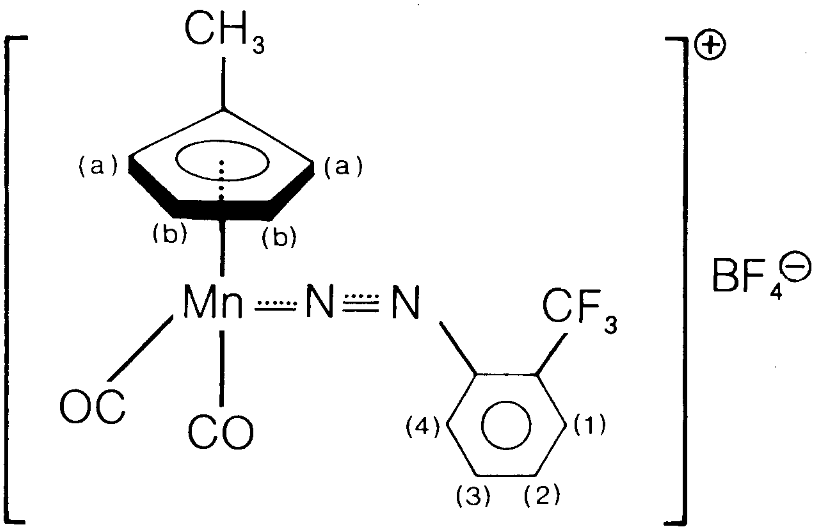
Although the infrared spectra of the complexes $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4R)]^+$ (R = CH_3, F, H) did not show much sensitivity to the substituents, observations on the syntheses, as noted above, showed that the stability of the complexes decreases in the order $CF_3 > F > H$ and that, qualitatively speaking, the rate of the reaction followed the same order.

Nuclear Magnetic Resonance

Although the ^{1}H-NMR spectra of many of the aryldiazenido complexes reported have been determined, the information they yield is very unspecific. It has been utilized as an analytical tool rather than as a probe into the electronic distribution in the complexes.

In this work, ^{1}H-NMR spectroscopy was especially useful to test if the aryldiazenido complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ has the same structure in solution as in the solid state, which was determined by x-ray studies.

The ^{1}H-NMR spectrum of this complex in $CDCl_3$, using tetramethylsilane as internal standard, showed peaks at (ppm): 2.05 (3H; CH_3), 5.74 (2H; H_a), 5.76 (2H; H_b), and three poorly resolved multiplets tentatively assigned to the aromatic protons (1-4) as: 8.30 (1H; H_1), 7.95 (1H, H_4) and 7.66 (2H, H_2 and H_3). The multiplet nature of these peaks is due to coupling between the aromatic protons and the fluorine atoms of the trifluoro-methyl group.



From these results, this manganese-aryldiazenido complex probably has the same structure in solution as in the solid state.

X-Ray Studies

Details of the molecular and crystal structure of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ will be presented in Chapter III.

2.3 EXPERIMENTAL

Substituted anilines were available commercially (Aldrich Chemical Company, Inc.) and were converted to diazonium tetrafluoroborate salts by standard procedures; these were then recrystallized from acetone/diethyl ether.

Methylcyclopentadienyl tricarbonyl manganese (Ventron, Alfa, Products) and triphenylsilane (Matheson, Coleman and Bell) were used directly as purchased.

All solvents were dried by usual methods and distilled under nitrogen. All reactions and manipulations were carried out under nitrogen.

Tetrahydrofuran (THF) was dried and purified just before use. It was distilled under N_2 over sodium-metal strips in the presence of benzophenone after 2-3h of reflux.

All photochemical reactions were carried out at atmospheric pressure in a Pyrex vessel (200 ml) equipped with a water cooled quartz finger joined to the vessel by a 60/50 standard taper joint. A 200 watt ultraviolet source (Hanovia high-pressure mercury N°654A36) was placed inside the quartz finger. Nitrogen was passed through the reaction vessel prior to the addition of the solvent and starting materials, and slow passage of nitrogen was maintained during the reaction.

Infrared spectra were recorded on Perkin-Elmer 457, Perkin-Elmer 599B and Perkin-Elmer 237 (fitted with external recorder) spectrometers calibrated against carbon monoxide or polystyrene film. A Varian XL-100 spectrometer was used to record the ^{1}H-NMR spectra.

Microanalyses were performed by Mr. M.K. Yang of the microanalytical laboratory of the Chemistry Department at Simon Fraser University.

a.) Methyl cyclopentadienyl dicarbonyl tetrahydrofuran manganese: $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2THF]$

This compound was prepared by published procedures.[30]

A solution of 2 ml of $(CH_3C_5H_4)Mn(CO)_3$ (0.0128 mol) and 150 ml of THF (distilled immediately before use) was irradiated for 1 h. A deep red coloured solution indicated the formation of the THF derivative.

The progress of the reaction was followed by monitoring the disappearance of the carbonyl band of the tricarbonyl complex (2018 cm^{-1}) and the appearance of the carbonyl band (1850 cm^{-1}) of the monosubstituted THF derivative in the i.r. spectrum of the reaction mixture.

I.R.: $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ in THF: ν(CO): 2018 vs, 1934 vs
$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2THF$: ν(CO): 1930 s, 1850 s.

b.) Reaction of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2THF$ with diazonium salts.

To a solution of 4 ml of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2THF$ in THF (prepared as above), solid diazonium salts [o-RC$_6$H$_4$N$_2$[[BF$_4$] (R ▫ CF$_3$, F, H) were added slowly at room temperature. Strong gas evolution immediately was noted and a yellow solution formed. No aryldiazenido complexes could be obtained from this solution. At low temperature (-35°C) the gas evolution was not so vigorous but, again, the solution became yellow and no aryldiazenido complexes could be obtained.

c.) Methyl cyclopentadienyl dicarbonyl cyclooctene manganese: $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(C_8H_{14})$.

A solution of 2.7 ml of $(CH_3C_5H_4)Mn(CO)_3$ (0.0173 mol) in 80 ml hexane and 25 ml of cyclooctene (0.19 mol) was irradiated for 4 h. After irradiation, some decomposition product was noted (brown solid). Filtration gave a deep yellow coloured solution from which the hexane was removed under vacuum (room temperature).

The remaining solution (~25 ml) was heated up to 80° C under high vacuum (diffusion pump). All the unreacted cyclooctene was removed, but the unreacted tricarbonyl was removed only partially under these conditions. The final product after this procedure was a dark brown oil with an i.r. spectrum (hexane) which showed the presence of the cyclooctene derivative: $\nu(CO)$ 1968 vs, 1907 vs cm^{-1} and $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ ($\nu(CO)$: 2022 vs, 1947 vs cm^{-1}) as the principal components.

d.) Reaction of the cyclooctene derivative with diazonium salts.

The brown oil was dissolved in hexane and a solution of the diazonium salt $[\underline{o}\text{-}RC_6H_4N_2][BF_4]$ (R = CF_3, F, H) in acetone was added at room temperature. A fast reaction took place to give a brown-red solution, accompanied by gas evolution.

The i.r. spectrum of the solution showed the presence of the aryldiazenido complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4R)][BF_4]$, but this could not be isolated as a solid even after addition of diethyl ether and cooling.

Also, the i.r. spectrum showed the presence of the tricarbonyl $(CH_3C_5H_4)Mn(CO)_3$ and cyclooctene derivative.

e.) Hydrido triphenylsilyl (η^5-methyl cyclopentadienyl) dicarbonyl manganese: $[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2Si(C_6H_5)_3]$

For the synthesis of this compound, a similar procedure to that reported previously was used.[31]

A mixture of 8 ml of $(CH_3C_5H_4)Mn(CO)_3$ (0.0512 mol) and 8.4 g of $HSiPh_3$ (0.0324 mol) in 150 ml of hexane was irradiated for 10 h. Very little decomposition product was noted. Yellow crystals precipitated out of the solution during the irradiation. These were collected and washed with cool hexane to remove the unreacted $(CH_3C_5H_4)Mn(CO)_3$. No further purification of the solid was necessary. Yield: 73%.

<u>Analysis</u>: Calculated for $(CH_3C_5H_4)MnH(CO)_2Si(C_6H_5)_3$

	C, 69.33;	H, 5.11
Found:	C, 69.18;	H, 5.20

I.R.: ν(CO) 1983 vs, 1926 vs cm^{-1} (in hexane)

The ν(Mn-H) was not observed.

<u>^{1}H-NMR:</u> (in $CDCl_3$) TMS internal standard; δ (ppm): 1.85 (singlet; 3H, CH_3); 4.25 (singlet; 2H) and 4.35 (singlet; 2H) protons of the cyclopentadienyl ring; 7.40 (br, doublet; 15H, $Si(C_6H_5)_3$ group) and -11.50 (singlet; 1H; Mn-H).

f.) <u>Synthesis of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$.</u>

To a solution of 135 mg of $(CH_3C_5H_4)MnH(CO)_2SiPh_3$ (0.3 mmol) in 20 ml of acetone was slowly added $[\underline{o}\text{-}CF_3C_6H_4N_2][BF_4]$ (78 mg; 0.3 mmol) and the mixture was stirred for 1 h at room temperature. The color of the solution changed from yellow to deep red. The solution was evaporated under vacuum at room temperature to approximately 2 ml. Diethyl ether was added carefully so as to precipitate only the unreacted diazonium salt and the reaction mixture was filtered under nitrogen. The clear deep red filtrate was allowed to cool slowly in the refrigerator at -12° C. Deep red-violet, needle-shaped crystals precipitated in 18% yield. M.P. = 114-115° C.

<u>Analysis</u>: Calculated for $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$

	C, 40.03;	H, 2.45;	N, 6.22
Found:	C, 39.70;	H, 2.48;	N, 6.20

The addition of diethyl ether to the reaction mixture has to be controlled very carefully. Excess of ether gives only an oily product, but on the other hand, if the amount of ether is not enough to complete the precipitation of the excess diazonium salt, no crystals are obtained.

Solutions of this aryldiazenido complex can be handled in air for a few minutes without observable deterioration, but decompose with longer exposure.

g.) Synthesis of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4F)][BF_4]$

This compound was synthesized by the same general method as described above.

To a solution of 135 mg of $(CH_3C_5H_4)MnH(CO)_2SiPh_3$ (0.3 mmol) in 20 ml of acetone, solid $[\underline{o}\text{-}FC_6H_4N_2][BF_4]$ was added (63 mg; 0.3 mmol) and the mixture was stirred for 1.5 h at room temperature. The color of the solution changed from yellow to very deep red-brown. The solution was concentrated under vacuum to approximately 2 ml. Addition of diethyl-ether was controlled very carefully and from the solution (which was more air-sensitive than the ortho-CF_3 derivative), crystals of the compound were obtained after four or five days at -78° C. These precipitated as small and very deep red-brownish air-sensitive crystals in 8% yield. M.P. = 117-118° C (in sealed capillary tube under vacuum).

Analysis:	Calculated for $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4F)][BF_4]$		
	C, 42.03	H, 2.75;	N, 7.01
Found:	C, 42.02;	H, 2.75;	N, 7.00

h.) Synthesis of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2C_6H_5)][BF_4]$

This compound was synthesized similarly. Its solutions were unstable and also very air-sensitive.

The 1:1 reaction mixture was stirred for 2.5 h at room temperature. The color of the solution changed from yellow to brown. The i.r. spectrum of this solution showed the presence of the manganese-aryldiazenido complex: $\nu(CO)$ 2078 vs, 2032 vs cm^{-1}.

No crystals of this compound could be obtained even at -78° C for several days.

CHAPTER III

MOLECULAR AND CRYSTAL STRUCTURE OF $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$

INTRODUCTION:

The study of the solid state structures of aryldiazenido complexes is of interest in view of the several attainable modes of bonding of the aryldiazo ligands to transition metals. As explained in Chapter I, these can coordinate in a singly-bent, doubly-bent, linear or bridging geometry.

The availability of well-formed crystals from the synthesis of the title complex, and the rather few known structures for manganese aryldiazenido complexes (and corresponding 3d metal aryldiazenido complexes in general) suggested a crystal structure determination to be particularly worthwhile. A particular objective was to confirm the proposed singly-bent geometry for the aryldiazenido ligand deduced previously from the ν(NN) frequency and electron-counting procedure. It should be noted that the presence of a relatively light metal is an advantage in permitting, in principle, a relatively accurate determination of the interesting non-metal atomic positions.

3.1 DETERMINATION OF THE STRUCTURE:

a) Crystal Mounting:

Crystals of η^5-methylcyclopentadienyl dicarbonyl ortho-trifluoromethyl phenyldiazenido manganese(0), tetrafluoroborate salt, were prepared by the method previously described in Chapter II. After recrystallization from acetone-ether, a well-formed single crystal (a parallelepiped of dimensions 0.16 × 0.31 × 0.11 mm) was chosen for use in the photographs and data collection and mounted along the long morphological axis on a thin glass fibre.

b.) Photography:

Oscillation photography was used for preliminary alignment, then Weissenberg photographs of the zero, first and second levels, and precession photographs of the zero, first and second levels of the other two axes were taken.

These photographs revealed the systematic absences:

$hk\ell$: $h+k,\ k+\ell,\ (\ell+h) = 2n+1$

$0k\ell$: $k+\ell = 4n+1,\ 4n+2,\ 4n+3\quad (k,\ell = 2n+1)$

$h0\ell$: $\ell+h = 4n+1,\ 4n+2,\ 4n+3\quad (\ell,h = 2n+1)$

$hk0$: $(h,k = 2n+1)$

$h00$: $(h = 4n+1,\ 4n+2,\ 4n+3)$

$0k0$: $(k = 4n+1,\ 4n+2,\ 4n+3)$

00ℓ: $(\ell = 4n+1,\ 4n+2,\ 4n+3)$

This allowed the space group to be unambiguously assigned as the orthorhombic group Fdd2. The approximate unit cell dimensions were $a = 12.85$, $b = 56.62$, $c = 9.91$ Å and $\alpha = \beta = \gamma = 90°$. The unit cell volume, calculated from the formula $V = a \times b \times c$, is 7210 $Å^3$.

The number of molecules per unit cell (Z) was calculated from the experimentally determined density and cell dimensions.

The theoretical value of the density (ρ) was calculated from the formula

$$\rho = \frac{(M)\ (Z)}{0.602\times(V)}$$

$$\rho = 1.653\ \text{g cm}^{-3}$$

where M is the gram formula weight (449.7 g), Z is the number of molecules per unit cell (16) and V is the unit cell volume.

The experimental value of the density was determined by flotation, using CCl_4 ($\rho = 1.59$ g cm^{-3}) and $CHBr_3$ ($\rho = 2.99$ g cm^{-3}). The crystal was placed in CCl_4 and $CHBr_3$ added dropwise until the crystal achieved zero buoyancy, the density of the crystal then being identical with that of the liquid mixture. Immediately, 5 ml of the liquid mixture were measured in a volumetric flask and weighed. The average density was 1.65 (±0.01) g cm^{-3}.

Data Collection:

The single crystal was mounted on a Picker FACS-1 computer-controlled diffractometer employing monochromatic $MoK_{\alpha 1}$ radiation.

Accurate cell dimensions were obtained by a least-squares analysis from the setting angles of 11 accurately centered reflections with $2\theta > 25°$. Crystal data are given in Table 1.

The intensities of 1318 unique reflections ($h,k,\ell \geq 0$) with $2\theta < 45°$ were measured and, of these, 1019 with $I > 2.3\sigma_I$ (σ_I is the standard deviation in the intensity derived from counter statistics and precision factor of 0.03) were regarded as observed and used in structure solution and refinement.

Data were collected at 291 K by a θ-2θ scan running at 2° min^{-1} with a scan range from 0.7° below K_{α_1} to 0.7° above K_{α_2}.

Stationary-crystal, stationary-counter 20 s background counts were measured. Two standard reflections were measured after every 50 data points, and showed no evidence of sample decomposition. No correction for absorption was made.

3.2 SOLUTION AND REFINEMENT

The x and y parameters for the manganese atom were determined from the three dimensional Patterson synthesis. (The z ccordinate was arbitrarily set at 0.25.)

Structure factor calculation gave R=0.57. A Fourier synthesis phased by this model revealed the location of most of the remaining non-hydrogen atoms (R=0.29).

A difference Fourier map of this stage revealed electron density in the vicinity of the CF_3 group which was interpreted as being an alternative orientation of the fluorine atoms.

In further refinement a disordered atom model was used: fluorine atoms of the original orientation were assigned population parameters of 0.7 and the second orientation 0.3. Subsequent refinement supported this assignment because the average temperature factors of the fluorine atoms of each orientation were very similar.

Mn, Cyclopentadienyl carbon atoms, O(1), O(2), fluorine atoms of the BF_4 group and fluorine atoms in the major orientation of the CF_3 group, were assigned anisotropic factors in further refinement.

The positions of the non-methyl hydrogen atoms were determined geometrically: angles C-C-H = 126°, 120° and $r_{C-H} = 0.95$ Å. The hydrogens of the methyl group were located in subsequent difference Fourier maps. The thermal parameters of the hydrogen atoms were set equal to the temperature factors of the carbon atoms to which they were attached. The methyl hydrogen coordinates were refined in future cycles. The scattering contributions of the other hydrogen atoms were included in all subsequent calculations, but these parameters were not refined.

The absolute configurations was tested by running a few cycles with atom coordinates transformed to (-x, -y, -z). A Hamilton R factor test revealed that this orientation improved the model more than 95% confidence level and was used subsequently.

A final difference Fourier synthesis map is essentially featureless with some peaks <0.40 eÅ^{-3} ($\sigma p = 0.12$ eÅ^{-3}). Their positions did not indicate that any further atoms should be assigned anisotropic temperature factors, so the refinement was finished.

All shift-to-error ratios were less than 0.1 in the final cycle. Final R = 0.055 ($R_w = 0.053$).

During the refinement, the quantity minimized was $\Sigma\, w\, (|F_o| - |F_c|)^2$, where w is a weighing scheme of the form

$w = {}^{1}/\sigma_F^2$. Neutral scattering factors were employed[49] and an anomalous dispersion[50] correction applied for Mn.

The atom-labelling scheme is shown in Figure 1 and the packing of the unit cell in Figure 2. Final atomic coordinates and thermal parameters are given in Table 4, inter-atomic distances and angles in Table 5, least squares planes in Table 6 and dihedral angles in Table 7. Observed and calculated structure factors are given in Table 8.

3.3 GENERAL DESCRIPTION OF THE STRUCTURE.

The structure of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ consists of discrete cations and anions with the geometry of the cation being of the "piano-stool" type.

A stereodrawing of the molecule is shown in Figure 3. A perspective view of the cation showing the inner coordination sphere, together with the more relevant bond distance and angles is shown in Figure 1.

The carbonyl ligands are essentially linear, as expected, with Mn-C-O angles averaging 178 (1)°.

The cyclopentadienyl ring shows slight departure from statistical planarity (χ^2 = 6.73, 4 degrees of freedom). The average Mn-C (cyclopentadienyl) distance is 2.138 (16) Å. The methyl group in the cyclopentadienyl ring is displaced out of the mean plane, away from the metal atom and the other ligands in the molecule (-0.064 Å).

The BF_4 anion is partially disordered (a common characteristic for BF_4 salts)[6], but the distortions from regular tetrahedral symmetry are not significant.

TABLE 3

CRYSTAL and X-RAY DATA

Formula: $C_{15}H_{11}BF_7MnN_2O_2$

MW: 449.7

Crystal System: orthorhombic

Space Group: Fdd2, C_{2v}^{19} 43

Unit Cell Dimensions: a = 12.866 (3)

b = 56.605 (11)

c = 9.964 (2)

$\alpha = \beta = \gamma = 90°$

V = 7256.6 Å^3

Z = 16

Crystal Dimensions: $0.16 \times 0.31 \times 0.11 = 5.5 \times 10^{-3}$ mm^3

$\rho_o = 1.65(1)$ g cm^{-3} (by flotation)

$\rho_c = 1.653$ g cm^{-3}

λ (MoK_{α_1}) = 0.70926 Å

μ (MoK_α) = 5.14 cm^{-1}

T = 291 ± 2° K

Reflections = 1318 ($h,k,\ell \geq 0$; $2\theta < 45°$)

Observed Reflections ($I > 2.3\,\sigma_I$) = 1019

Total Parameters = 208

$R_1 = 0.055$

$R_2 = 0.053$

TABLE 4

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	x	y	z	U
Mn	0.28658(12)	0.54128(2)	0.75000(-)	*
C(1)	0.17797(98)	0.53247(21)	0.85485(129)	55(3)
O(1)	0.11148(67)	0.52659(15)	0.92435(98)	*
C(2)	0.20234(100)	0.53822(20)	0.60139(130)	59(3)
O(2)	0.15233(64)	0.53641(14)	0.50697(112)	*
N(1)	0.27793(59)	0.57086(12)	0.77276(90)	43(2)
N(2)	0.28190(63)	0.59221(12)	0.77760(86)	44(2)
C(3)	0.26365(70)	0.60594(16)	0.89118(102)	36(3)
C(4)	0.23944(79)	0.59546(17)	1.01062(129)	55(3)
C(5)	0.21702(107)	0.60929(22)	1.12653(141)	75(4)
C(6)	0.22258(105)	0.63368(23)	1.11153(146)	77(4)
C(7)	0.25038(84)	0.64414(18)	0.99534(148)	62(3)
C(8)	0.27339(80)	0.63065(18)	0.88095(109)	41(3)
C(9)	0.31107(97)	0.64193(20)	0.75438(170)	60(3)
C(10)	0.37962(104)	0.51644(23)	0.86148(139)	*
C(11)	0.36024(79)	0.50826(16)	0.73212(174)	*
C(12)	0.40650(89)	0.52356(20)	0.64061(125)	*
C(13)	0.45099(76)	0.54234(17)	0.71190(95)	*
C(14)	0.43269(100)	0.53742(23)	0.85052(116)	*
C(15)	0.51282(121)	0.56288(26)	0.65567(156)	75(4)
F(1)	0.25541(193)	0.64112(47)	0.66641(198)	*
F(2)	0.34417(127)	0.66400(17)	0.78038(130)	*
F(3)	0.39433(105)	0.63122(22)	0.70197(142)	*

continuation TABLE 4

F(4)	0.25742(270)	0.66185(56)	0.73813(342)	98(10)
F(5)	0.39981(293)	0.64439(74)	0.75008(431)	106(12)
F(6)	0.24836(323)	0.63678(79)	0.62786(450)	98(14)
B	-0.14631(130)	0.54220(34)	0.74893(267)	78(4)
F(7)	-0.15100(76)	0.52247(13)	0.81468(102)	*
F(8)	-0.22221(81)	0.54398(17)	0.65393(110)	*
F(9)	-0.05501(83)	0.54776(18)	0.68758(126)	*
F(10)	-0.15637(132)	0.55979(19)	0.83706(143)	*

* ANISOTROPIC TEMPERATURE FACTORS IN THE FORM

$$\exp[-2\pi^2(\underline{U}_{11}\underline{h}^2\underline{a}^{*2} + \dots\dots 2\underline{U}_{23}\underline{k}\,\underline{\ell}\,\underline{b}^*\,\underline{c}^*)]$$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	398(7)	292(7)	449(8)	14(8)	25(9)	-29(9)
O(1)	787(64)	874(64)	974(79)	-76(52)	375(64)	9(58)
O(2)	798(61)	1021(67)	867(64)	279(50)	-426(62)	-367(69)
C(10)	702(89)	568(83)	549(89)	41(71)	159(76)	153(73)
C(11)	432(66)	229(53)	1062(119)	102(49)	156(80)	46(79)
C(12)	510(76)	429(73)	519(79)	86(62)	-2(66)	-169(65)
C(13)	302(55)	389(58)	453(84)	96(52)	0(51)	-72(62)
C(14)	599(88)	735(101)	380(75)	229(74)	-85(66)	-37(74)
F(1)	2165(202)	2589(253)	909(129)	-1842(183)	-1165(136)	1103(158)
F(2)	1625(117)	364(54)	1150(105)	-663(67)	163(101)	-71(62)
F(3)	1161(102)	727(74)	947(105)	209(78)	571(83)	255(75)
F(7)	1596(90)	787(61)	1586(88)	-305(61)	-386(73)	587(60)
F(8)	1411(87)	1415(88)	1370(83)	17(71)	-444(79)	579(78)

continuation TABLE 4

F(9)	1405(89)	1362(89)	1755(116)	-385(72)	350(85)	-61(78)
F(10)	3081(175)	1405(96)	1629(121)	-737(103)	676(126)	-226(91)

HYDROGEN ATOMS

Atom	x	y	z	U
H(1)	0.487(8)	0.563(2)	0.568(10)	75
H(2)	0.500(7)	0.576(2)	0.725(10)	75
H(3)	0.596(9)	0.561(2)	0.643(10)	75
H(4)	0.360	0.510	0.944	58
H(5)	0.323	0.495	0.712	59
H(6)	0.408	0.522	0.545	50
H(7)	0.456	0.548	0.922	58
H(8)	0.238	0.578	1.015	55
H(9)	0.199	0.602	1.209	75
H(10)	0.207	0.643	1.187	79
H(11)	0.255	0.661	0.992	63

TABLE 5

SELECTED INTERATOMIC DISTANCES IN Å FOR $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$

				corrected
Mn - C(1)	1.815(13)	C(12) - C(13)	1.401(14)	
Mn - C(2)	1.843(13)	C(13) - C(14)	1.428(16)	
Mn - N(1)	1.693(7)	C(13) - C(15)	1.516(17)	
Mn - C(10)	2.155(13)	C(1) - O(1)	1.150(12)	1.196(16)
Mn - C(11)	2.104(9)	C(2) - O(2)	1.144(14)	1.191(17)
Mn - C(12)	2.139(11)	C(9) - F(1)	1.133(22)	1.319(27)
Mn - C(13)	2.150(10)	C(9) - F(2)	1.337(16)	1.413(16)
Mn - C(14)	2.141(12)	C(9) - F(3)	1.345(14)	1.375(19)
N(1)-N(2)	1.211(8)	C(9) - F(4)	1.332(26)	1.360(34)
N(2)-C(3)	1.393(12)	C(9) - F(5)	1.151(35)	1.191(39)
C(3)-C(4)	1.366(15)	C(9) - F(6)	1.525(44)	1.550(46)
C(3)-C(8)	1.408(13)	B - F(7)	1.296(21)	1.371(22)
C(4)-C(5)	1.425(16)	B - F(8)	1.364(22)	1.428(24)
C(5)-C(6)	1.391(16)	B - F(9)	1.361(19)	1.431(22)
C(6)-C(7)	1.349(17)	B - F(10)	1.334(23)	1.455(25)
C(7)-C(8)	1.404(15)			
C(8)-C(9)	1.495(17)			
C(10)-C(11)	1.392(17)			
C(10)-C(14)	1.374(17)			
C(11)-C(12)	1.391(16)			

continuation TABLE 5

SELECTED ANGLES IN DEGREES FOR

$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2(\underline{o}\text{-N}_2\text{C}_6\text{H}_4\text{CF}_3)][\text{BF}_4]$

Mn - N(1) - N(2)	171.8(8)
Mn - C(1) - O(1)	177.7(12)
Mn - C(2) - O(2)	178.2(12)
N(1) - Mn - C(1)	98.3(5)
N(1) - Mn - C(2)	99.3(5)
N(1) - Mn - C(10)	127.8(5)
N(1) - Mn - C(11)	156.9(4)
N(1) - Mn - C(12)	125.4(4)
N(1) - Mn - C(13)	93.5(4)
N(1) - Mn - C(14)	95.5(4)
N(1) - N(2) - C(3)	125.6(9)
N(2) - C(3) - C(4)	120.3(8)
N(2) - C(3) - C(8)	118.7(9)
C(1) - Mn - C(2)	89.1(6)
C(1) - Mn - C(10)	87.2(5)
C(1) - Mn - C(11)	98.7(5)
C(1) - Mn - C(12)	136.0(5)
C(1) - Mn - C(13)	150.1(5)
C(1) - Mn - C(14)	112.3(5)
C(2) - Mn - C(10)	132.8(6)
C(2) - Mn - C(11)	96.5(6)
C(2) - Mn - C(12)	88.3(5)
C(2) - Mn - C(13)	116.1(5)
C(2) - Mn - C(14)	151.9(5)
C(3) - C(4) - C(5)	121.0(9)
C(4) - C(5) - C(6)	116.6(12)
C(5) - C(6) - C(7)	122.8(13)
C(6) - C(7) - C(8)	120.9(10)
C(7) - C(8) - C(9)	121.4(10)
C(3) - C(8) - C(9)	121.0(10)
C(10)- C(11)- C(12)	108.8(10)
C(10)- C(14)- C(13)	109.1(11)
C(11)- C(10)- C(14)	107.6(11)
C(11)- C(12)- C(13)	108.4(11)
C(12)- C(13)- C(14)	106.0(11)
C(12)- C(13)- C(15)	127.5(10)
C(14)- C(13)- C(15)	126.4(10)
C(8) - C(9) - F(1)	115.5(14)
C(8) - C(9) - F(2)	109.7(12)
C(8) - C(9) - F(3)	113.3(11)
F(1) - C(9) - F(2)	112.7(16)
F(1) - C(9) - F(3)	100.7(20)
F(2) - C(9) - F(3)	104.1(12)

continuation TABLE 5

F(7) - B - F(8) : 112.4(16)

F(7) - B - F(9) : 117.8(15)

F(7) - B - F(10): 107.8(20)

F(8) - B - F(9) : 106.8(19)

F(8) - B - F(10): 109.4(15)

F(9) - B - F(10): 101.9(15)

C(4) - C(3)- C(8) : 121.0(10)

C(3) - C(8)- C(7) : 117.6(10)

TABLE 6

DEVIATIONS FROM LEAST-SQUARES PLANES CALCULATED FOR $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]^*$

---

a) Plane through C(10), C(11), C(12), C(13) and C(14)

$-0.8590\underline{x} + 0.5089\underline{y} - 0.0425\underline{z} - 10.3269 = 0 \quad \chi^2 = 6.73$

C(10)	-0.015	C(11)	0.018	C(12)	-0.014
C(13)	0.005	C(14)	0.007	C(15)	-0.064

b) Plane through C(10), C(11), C(12), C(13), C(14) and C(15)

$-0.8524\underline{x} + 0.5206\underline{y} - 0.0480\underline{z} - 10.6702 = 0 \quad \chi^2 = 14.90$

C(10)	-0.026	C(11)	0.008	C(12)	-0.005
C(13)	0.026	C(14)	0.016	C(15)	-0.019

c) Plane through C(3), C(4), C(5), C(6), C(7) and C(8)

$-0.9640\underline{x} + 0.0381\underline{y} - 0.2633\underline{z} + 4.3257 = 0 \quad \chi^2 = 12.44$

C(3)	0.024	C(4)	-0.012	C(5)	-0.008
C(6)	0.015	C(7)	-0.003	C(8)	-0.017

[*] Deviations of atoms from the planes are given in Å.

TABLE 7

DIHEDRAL ANGLES

PLANES

a)	Mn - N(1) - N(2) N(1)-N(2) - C(3)	145.0(51)
b)	N(1) - N(2) - C(3) N(2) - C(3) - C(4)	-0.4(15)
c)	N(1) - N(2) - C(3) N(2) - C(3) - C(8)	-178.7(10)

TABLE 8

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$

K	FO	FC	ALPHA
H=	0, L=	0	
8	62	67	184
12	1011	1008	180
16	561	549	180
20	185	173	1
24	216	216	2
28	243	235	1
32	133	141	181
36	206	210	182
40	200	201	181
44	145	141	1
48	184	176	2
52	48	51	4
56	28*	26	185
60	145	137	182
H=	2, L=	0	
2	363	372	181
4	354	341	0
6	2*	19	180
8	506	481	0
10	285	267	1
12	120	119	179
14	204	196	2
16	30	23	349
18	200	194	0
20	50	43	354
22	322	320	181
24	252	254	359
26	124	134	183
28	95	99	2
30	193	191	180
32	135	129	1
34	215	211	1
36	102	104	179
38	177	170	2
40	151	145	181
42	10*	8	174
44	60	59	183
46	64	72	184
48	4*	9	357
50	41	52	186
52	56	67	2
54	76	67	180
56	91	93	1
58	77	72	3
60	5*	0	245
H=	4, L=	0	
0	318	328	1
2	132	130	181
4	542	541	179
6	50	53	189
8	192	188	180
10	165	153	358
12	165	166	182
14	5*	9	154
16	10*	15	192
18	29	18	153
20	312	297	0
22	11*	14	17
24	157	152	2
26	75	75	182
28	229	228	0
30	68	71	185
32	90	98	181
34	46	45	185
36	153	154	181
38	45	42	3
40	61	64	182
42	112	107	3
44	63	63	1
46	32*	30	6
48	69	65	3
50	76	79	181
52	38	44	3
54	45	53	185
56	5*	6	193
58	48	43	183
H=	6, L=	0	
2	26	17	185
4	347	350	1
6	47	41	359
8	191	197	2
10	33*	40	2
12	68	70	179
14	8*	8	12
16	275	282	181
18	106	109	0
20	346	339	181
22	112	112	180
24	36	26	181
26	44	40	357
28	137	132	3
30	4*	7	358
32	160	158	2
34	79	72	0
36	15*	13	2
38	33	21	176
40	158	161	182
42	7*	13	178
44	73	80	184
46	46	51	181
48	38	27	358
50	11*	2	141
52	59	59	4
54	36	22	180
H=	8, L=	0	
0	60	64	357
2	154	156	181
4	97	98	180
6	148	154	183
8	131	131	0
10	88	82	182
12	140	138	0
14	96	91	2
16	50	52	1
18	122	123	3
20	32	39	181
22	119	116	2
24	144	139	180
26	8*	15	192
28	62	66	180
30	94	96	184
32	16*	18	3
34	87	89	182
36	4*	29	3
38	52	64	2
40	5*	22	2
42	97	94	3
44	5*	8	185
46	44	41	4
48	5*	34	182
50	5*	2	106
H=	10, L=	0	
2	52	57	4
4	123	124	2
6	4*	14	179
8	68	66	4
10	57	53	184
12	4*	14	0
14	46	42	185
16	62	62	184
18	30*	48	180

```
 K    FO     FC  ALPHA

 20    70     70    183
 22    31*    11     19
 24     4*    18    358
 26    35     21     10
 28    93     88      2
 30    19*     4      2
 32   111    112      2
 34    29*    12    196
 36     5*    13    177
 38    42     30    186
 40    51     41    184
 42    29*     3    184
 44    64     64    183
 46    55     50      3
 48     5*     7    355
 50    35*    26      6

H=   12, L=    0

  0   106    105    182
  2    47     56    181
  4    67     62    182
  6    78     85    181
  8    58     47      3
 10    19*    23    182
 12    98     91      3
 14    43     23      2
 16    17*    28      5
 18    32*    39      3
 20    49     37    183
 22    39     34      1
 24   107    105    182
 26     5*    26    181
 28    30*    21    187
 30    40     48    182
 32    44     42      2
 34    44     52    181
 36   100     96      2
 38    17*     1     62
 40    27*    41      3

H=   14, L=    0

  2    67     73      3
  4    27*     7    182
  6    36*    16    179
  8    20*    18    180
 10    45     42    185
 12    14*    12      0
 14    44     48    184
 16    16*    11      1
```

```
 K    FO     FC  ALPHA

 18     7*     8    358
 20     5*    13      1
 22    46     55      3
 24    18*    18    180
 26    49     60      3

H=   15, L=    1

  1     5*     6    132
  3    45     39    109
  5     5*    26    252
  7    17*    21    112
  9     5*    19    178
 11    18*     2     16

H=   13, L=    1

  1    19*    23    215
  3    64     51    217
  5    74     74    127
  7    64     59     53
  9    29*    26    152
 11    14*     7    243
 13    18*     9     62
 15    44     39    220
 17    39     44    307
 19    50     53    211
 21    29*    34    335
 23    15*    10    249
 25     9*    24    176
 27    60     56    225
 29    40*    46    161
 31    71     62     22
 33    56     59    136

H=   11, L=    1

  1    90     99    161
  3    51     54    359
  5    75     85    241
  7    57     61    136
  9    36     50    250
 11    15*    38    114
 13    44     51    343
 15    35     37    200
 17    54     47     22
 19    56     55    108
 21    63     70    249
 23    46     43    223
 25    55     59    155
 27    51     48      2
```

```
 K    FO     FC  ALPHA

 29    71     54    192
 31    10*    23    340
 33    40     40    269
 35    55     62    239
 37    47     40    339
 39    53     60    160
 41    56     53     16
 43    40     31    153
 45    12*    29     90

H=    9, L=    1

  1   143    149    212
  3    81     83    355
  5    91     87    120
  7   108     99     77
  9    64     62    115
 11    88     81    111
 13    90     86     26
 15    29*    28    213
 17    69     61    342
 19    77     74    214
 21    77     82    307
 23    68     78    114
 25    36     36    271
 27    25*    12    329
 29    35     44    195
 31     4*    13     24
 33    42     42    249
 35    85     81    132
 37    39     37     56
 39    48     56    179
 41    41     42    344
 43    34*    45    237
 45    70     59    253

H=    7, L=    1

  1   259    269    133
  3    77     79    129
  5    32     39    107
  7    65     67    104
  9    83     83     13
 11   187    193    228
 13   136    141    144
 15   144    150    201
 17   133    137    340
 19    70     68    157
 21    85     85    117
 23   103    108    245
 25    78     67    154
```

H= 7, L= 1

K	FO	FC	ALPHA
27	98	104	28
29	89	91	162
31	30*	28	102
33	53	63	307
35	107	103	244
37	101	98	304
39	46	52	215
41	18*	27	1
43	39	41	16
45	75	76	137
47	98	95	249
49	59	54	136
51	58	56	219

H= 5, L= 1

K	FO	FC	ALPHA
1	139	139	277
3	193	199	110
5	220	227	359
7	132	132	153
9	135	135	213
11	94	95	187
13	107	104	103
15	120	116	150
17	113	118	167
19	89	87	57
21	151	156	186
23	151	152	336
25	83	80	213
27	56	61	342
29	74	75	254
31	59	49	244
33	119	118	211
35	64	67	160
37	90	93	250
39	118	120	89
41	47	47	117
43	89	90	20
45	74	83	196
47	70	72	338
49	53	53	246
51	17*	28	106
53	51	53	280
55	67	41	243

H= 3, L= 1

K	FO	FC	ALPHA
1	266	267	115
3	386	393	192
5	200	200	350
7	346	329	228
9	77	72	120
11	169	165	308
13	103	107	193
15	127	132	138
17	158	165	233
19	157	149	358
21	164	167	176
23	138	134	247
25	126	124	157
27	113	113	102
29	81	75	250
31	113	115	160
33	147	149	354
35	76	81	228
37	82	88	346
39	135	144	107
41	60	64	239
43	79	81	341
45	35	38	215
47	12*	11	335
49	29*	46	149
51	11*	27	141
53	5*	14	229
55	55	49	137
57	5*	34	214
59	53	55	189

H= 1, L= 1

K	FO	FC	ALPHA
1	258	246	130
3	337	355	247
5	83	83	242
7	222	221	218
9	287	278	130
11	72	81	261
13	23	11	282
15	196	192	252
17	103	101	154
19	331	319	56
21	140	135	129
23	257	244	13
25	148	148	304
27	14*	9	260
29	132	130	107
31	276	281	240
33	162	170	338
35	161	157	185
37	23*	32	80
39	79	77	123
41	149	153	116
43	51	63	217
45	62	62	145
47	33*	43	351
49	22*	24	265
51	40	30	226
53	49	46	276
55	15*	41	221
57	100	98	333
59	59	50	157

H= 0, L= 2

K	FO	FC	ALPHA
2	622	600	187
6	110	107	211
10	607	600	337
14	142	127	53
18	114	111	147
22	367	368	136
26	164	169	160
30	38	34	247
34	288	291	349
38	195	202	352
40	15*	0	2
42	44	48	162
44	4*	0	104
46	134	132	165
48	4*	0	134
50	89	99	171
52	4*	0	204
54	37	32	240
56	5*	0	24
58	94	104	349

H= 2, L= 2

K	FO	FC	ALPHA
0	329	327	5
2	517	509	192
4	133	129	21
6	398	393	176
8	230	228	219
10	322	312	163
12	149	137	123
14	21*	28	272
16	130	125	145
18	180	180	347
20	79	76	112
22	136	142	138
24	208	200	334
26	100	98	174
28	91	102	141

K	FO	FC	ALPHA
30	131	123	186
32	85	94	129
34	58	59	195
36	128	128	182
38	26*	30	295
40	101	92	156
42	125	124	24
44	84	81	357
46	51	56	63
48	82	87	18
50	44	53	152
52	50	43	138
54	67	53	168
56	15*	12	194
58	36*	49	196
H=	4, L=	2	
2	279	282	137
4	264	265	17
6	172	169	213
8	161	167	9
10	264	266	138
12	38	38	88
14	224	220	357
16	108	107	171
18	39	48	133
20	136	138	166
22	85	88	200
24	23*	19	112
26	183	193	188
28	83	89	140
30	29*	36	216
32	153	155	358
34	55	55	20
36	82	83	130
38	94	104	339
40	151	145	184
42	39	19	114
44	50	50	200
46	80	83	194
48	56	45	116
50	56	53	138
52	49	49	9
54	19*	15	223
56	88	88	24
H=	6, L=	2	
0	72	75	275
2	207	213	215

K	FO	FC	ALPHA
4	36	46	332
6	255	260	150
8	70	72	188
10	65	57	102
12	131	134	160
14	151	151	4
16	36	35	94
18	265	266	355
20	11*	19	109
22	117	119	18
24	90	92	7
26	101	107	142
28	42	43	221
30	194	190	181
32	23*	21	96
34	82	87	196
36	72	76	214
38	90	96	348
40	38	22	213
42	147	146	358
44	28*	36	303
46	41	44	358
48	5*	7	118
50	7*	25	194
52	45	36	352
H =	8, L=	2	
2	63	61	339
4	155	163	1
6	4*	11	186
8	73	70	305
10	90	86	213
12	27*	26	173
14	78	82	154
16	73	67	210
18	51	59	216
20	148	149	193
22	74	73	19
24	6*	14	221
26	18*	22	211
28	57	55	215
30	38	43	250
32	106	110	218
34	34	38	80
36	21*	16	212
38	46	49	214
40	101	95	166
42	27*	33	0
44	68	75	209
46	25*	25	305

K	FO	FC	ALPHA
48	5*	5	84
H=	10, L=	2	
0	88	102	165
2	89	105	219
4	36	38	335
6	125	117	167
8	32*	18	22
10	46	48	217
12	66	64	351
14	17*	3	342
16	58	50	7
18	84	75	348
20	31*	35	197
22	59	49	344
24	36	30	224
26	40	52	160
28	55	50	179
30	67	57	178
32	25*	12	8
34	76	71	180
36	49	47	11
38	45	40	359
40	26*	17	356
H=	12, L=	2	
2	94	95	359
4	83	85	10
6	16*	20	159
8	32*	29	15
10	75	67	173
12	16*	35	59
14	81	74	153
16	33*	39	171
18	15*	12	243
20	24*	33	205
22	81	89	354
24	5*	14	261
26	76	71	337
28	27*	44	137
H=	13, L=	3	
1	36*	35	269
3	55	65	336
5	39	43	205
7	66	56	111
9	34*	33	247
11	26*	30	359

H= 11, L= 3

K	FO	FC	ALPHA
1	46	54	232
3	77	84	4
5	50	56	152
7	35	31	94
9	54	57	251
11	27*	11	28
13	30*	31	349
15	71	77	177
17	48	39	310
19	66	68	234
21	42	40	261
23	5*	12	245
25	57	59	205
27	37	38	336
29	37	50	137
31	62	61	220

H= 9, L= 3

K	FO	FC	ALPHA
1	109	104	181
3	107	112	218
5	50	48	170
7	67	72	249
9	95	104	114
11	79	69	230
13	79	73	352
15	46	51	224
17	79	81	15
19	44	62	166
21	53	53	113
23	93	89	225
25	90	75	149
27	54	54	55
29	43	44	225
31	36	29	140
33	25*	11	261
35	35*	40	234
37	99	100	339
39	67	60	199
41	32*	30	52
43	52	50	82

H= 7, L= 3

K	FO	FC	ALPHA
1	198	211	252
3	117	120	356
5	8*	19	141
7	117	120	148
9	131	134	90
11	115	116	133
13	142	141	252
15	125	129	140
17	72	72	53
19	59	59	138
21	63	69	250
23	108	113	333
25	110	110	242
27	118	121	131
29	40	26	266
31	37	41	88
33	75	74	3
35	114	114	159
37	110	115	60
39	97	87	146
41	4*	13	16
43	29*	22	277
45	66	63	229
47	69	71	133
49	71	67	201

H= 5, L= 3

K	FO	FC	ALPHA
1	142	151	132
3	139	135	252
5	226	234	89
7	140	146	182
9	184	186	146
11	125	124	208
13	139	142	141
15	73	77	248
17	64	65	111
19	110	107	108
21	162	158	177
23	132	120	223
25	162	158	145
27	97	97	226
29	37	58	245
31	38	30	165
33	75	78	352
35	61	65	215
37	178	170	132
39	127	130	249
41	99	100	209
43	68	73	13
45	28*	46	204
47	20*	23	254
49	104	99	141
51	49	55	221
53	52	40	110

H= 3, L= 3

K	FO	FC	ALPHA
1	244	242	216
3	293	297	252
5	217	211	307
7	280	284	210
9	166	163	20
11	33	29	84
13	188	188	337
15	183	179	126
17	127	127	84
19	193	194	17
21	128	125	187
23	103	110	9
25	93	93	221
27	95	104	279
29	97	103	245
31	79	74	256
33	26*	30	212
35	91	101	176
37	55	54	110
39	105	105	92
41	108	106	118
43	57	74	224
45	13*	14	179
47	53	56	148
49	23*	16	141
51	27*	25	259
53	17*	42	148
55	32*	48	250
57	52	48	1

H= 1, L= 3

K	FO	FC	ALPHA
1	263	272	247
3	160	155	162
5	167	168	121
7	95	92	138
9	54	57	337
11	172	177	264
13	107	100	211
15	147	153	356
17	251	263	278
19	92	94	143
21	146	150	234
23	170	164	55
25	80	73	121
27	147	146	141
29	204	204	79
31	137	135	158
33	174	176	64

K	FO	FC	ALPHA
35	46	41	158
37	57	47	23
39	109	108	281
41	159	145	230
43	69	79	349
45	45	30	332
47	34	36	133
49	34	15	63
51	47	47	96
53	55	65	2
55	80	83	126
57	52	49	13
H=	0, L=	4	
0	210	219	341
4	47	51	59
8	277	237	199
12	183	181	64
16	256	249	203
20	274	270	335
24	277	288	355
28	96	104	355
32	111	114	136
36	217	223	181
40	103	100	211
44	70	66	355
48	79	86	348
52	44	46	220
56	37*	47	121
H=	2, L=	4	
2	272	259	214
4	18*	34	57
6	103	104	252
8	90	96	22
10	166	171	9
12	82	91	140
14	78	82	23
16	78	81	132
18	26*	26	59
20	128	130	131
22	101	92	173
24	78	73	103
26	134	132	168
28	108	111	144
30	40	44	106
32	135	133	335
34	32	36	4
36	30*	34	5

K	FO	FC	ALPHA
38	224	217	9
40	61	70	210
42	116	102	193
44	26*	19	128
46	11*	23	212
48	10*	19	265
50	104	94	181
52	36*	35	12
54	5*	22	225
H=	4, L=	4	
0	98	99	145
2	156	160	211
4	133	128	355
6	194	198	187
8	189	177	164
10	76	86	152
12	43	44	226
14	11*	6	197
16	150	148	170
18	159	165	2
20	68	71	109
22	96	94	344
24	37	45	222
26	36	46	225
28	24*	15	182
30	146	148	176
32	40	47	91
34	50	56	156
36	97	100	190
38	32*	41	254
40	4*	28	220
42	108	105	16
44	47	46	5
46	17*	37	352
48	46	54	143
50	39	31	219
52	37	47	16
H=	6, L=	4	
2	37	45	58
4	226	227	350
6	95	94	220
8	173	181	329
10	60	77	102
12	41	36	103
14	63	58	222
16	130	131	156
18	35	25	266

K	FO	FC	ALPHA
20	139	143	179
22	18*	18	224
24	46	42	181
26	19*	30	241
28	95	89	351
30	4*	6	339
32	89	92	11
34	36	30	194
36	70	61	55
38	65	62	27
40	133	127	180
42	5*	25	152
44	83	83	179
46	31*	14	216
48	18*	20	163
50	30*	11	144
H=	8, L=	4	
0	59	51	251
2	86	82	177
4	39	28	28
6	120	124	193
8	22*	26	246
10	30*	40	153
12	49	47	30
14	69	64	336
16	41	38	170
18	120	127	15
20	14*	25	111
22	79	80	4
24	4*	14	53
26	4*	17	161
28	34	30	267
30	110	107	192
32	60	55	347
34	78	73	209
36	5*	18	113
38	5*	31	10
40	25*	13	217
42	92	86	355
44	21*	26	143
H=	10, L=	4	
2	14*	14	112
4	98	101	10
6	21*	28	195
8	55	57	354
10	47	39	203
12	23*	7	156

H= 10, L= 4

K	FO	FC	ALPHA
14	4*	20	210
16	67	69	160
18	16*	14	247
20	52	49	165
22	69	67	217
24	5*	28	215
26	43	45	221
28	68	73	355
30	11*	6	244
32	62	58	341
34	52	41	199

H= 12, L= 4

K	FO	FC	ALPHA
0	92	78	188
2	27*	9	18
4	49	55	172
6	37	43	172
8	50	47	0
10	5*	16	218
12	65	62	351
14	5*	13	240
16	43	41	1
18	11*	5	309
20	29*	23	187

H= 11, L= 5

K	FO	FC	ALPHA
1	38	36	159
3	90	80	354
5	49	53	238
7	63	60	295
9	47	36	273
11	5*	10	334
13	27*	16	300
15	52	56	172
17	53	55	61
19	61	55	128
21	42	47	253
23	32*	12	94

H= 9, L= 5

K	FO	FC	ALPHA
1	30*	46	207
3	42	53	9
5	17*	24	242
7	67	70	147
9	68	54	256
11	69	66	132
13	60	60	349
15	47	43	171
17	33*	31	10
19	73	57	259
21	71	55	248
23	77	76	143
25	78	77	209
27	53	60	346
29	55	51	165
31	40	38	93
33	23*	16	215
35	51	55	135

H= 7, L= 5

K	FO	FC	ALPHA
1	120	117	148
3	89	91	220
5	44	52	97
7	78	79	218
9	125	133	306
11	88	75	203
13	87	89	115
15	78	84	210
17	64	67	111
19	47	49	24
21	67	73	143
23	96	95	9
25	75	74	125
27	47	45	220
29	39	41	103
31	9*	20	107
33	54	45	144
35	98	105	206
37	78	87	142
39	55	41	198
41	19*	21	135
43	15*	30	101

H= 5, L= 5

K	FO	FC	ALPHA
1	189	190	229
3	215	217	110
5	43	55	135
7	32	41	232
9	102	108	216
11	92	102	131
13	148	141	221
15	146	140	92
17	139	135	252
19	51	55	98
21	68	57	196
23	106	109	339
25	90	91	232
27	93	92	269
29	77	65	280
31	61	62	186
33	42	41	11
35	36	38	181
37	108	107	246
39	102	93	116
41	54	53	153
43	77	78	359
45	26*	27	152
47	45	47	142
49	74	69	214

H= 3, L= 5

K	FO	FC	ALPHA
1	171	173	130
3	68	71	117
5	190	200	253
7	143	156	178
9	146	148	358
11	91	100	209
13	34	30	28
15	138	146	268
17	90	93	227
19	113	122	4
21	73	65	213
23	75	74	3
25	86	86	156
27	117	117	102
29	93	87	256
31	94	95	125
33	57	56	51
35	76	76	201
37	55	52	114
39	100	99	306
41	103	103	255
43	60	55	147
45	51	46	196
47	33*	41	358
49	35	22	122
51	38	30	79

H= 1, L= 5

K	FO	FC	ALPHA
1	94	90	301
3	183	177	214
5	197	190	146
7	202	199	220
9	83	78	250

K	FO	FC	ALPHA
11	157	151	121
13	32	44	127
15	53	54	3
17	188	186	153
19	121	124	228
21	98	95	185
23	77	72	333
25	38	31	275
27	80	82	265
29	105	112	132
31	110	96	211
33	95	91	333
35	47	34	300
37	47	49	14
39	99	88	92
41	97	100	166
43	76	79	9
45	52	56	79
47	39	23	165
49	31*	32	257
51	42	60	220
53	44	39	134

H= 0, L= 6

K	FO	FC	ALPHA
2	72	79	166
6	20*	33	106
10	74	72	351
14	115	123	345
18	20*	26	123
22	130	129	154
26	159	155	173
30	4*	30	193
34	141	141	351
38	91	90	20
42	64	61	278
46	69	70	179
50	46	52	200

H= 2, L= 6

K	FO	FC	ALPHA
0	209	202	214
2	50	61	169
4	86	81	359
6	30	29	215
8	118	118	201
10	52	50	84
12	135	136	199
14	79	87	112
16	41	44	203
18	123	121	10
20	37	33	357
22	36	35	29
24	161	158	21
26	50	44	138
28	74	74	22
30	125	127	161
32	64	52	216
34	54	64	172
36	115	115	196
38	19*	9	188
40	81	84	209
42	32*	42	355
44	57	56	221
46	32*	26	330
48	71	78	0

H= 4, L= 6

K	FO	FC	ALPHA
2	111	104	198
4	153	160	23
6	36	36	210
8	142	151	20
10	45	43	7
12	38	46	144
14	129	128	340
16	101	100	187
18	33	36	98
20	140	141	199
22	33	38	231
24	36	27	171
26	75	70	181
28	82	81	8
30	31*	34	223
32	93	100	17
34	75	79	352
36	18*	36	226
38	64	50	60
40	84	86	212
42	38	38	24
44	34*	40	176
46	45	60	165

H= 6, L= 6

K	FO	FC	ALPHA
0	44	37	297
2	94	104	179
4	51	51	215
6	90	97	178
8	39	35	191
10	57	65	142
12	36	39	139
14	51	51	109
16	4*	5	105
18	68	85	341
20	48	46	200
22	35	45	341
24	34	21	307
26	17*	9	159
28	4*	20	53
30	62	61	163
32	26*	32	29
34	49	42	212
36	5*	16	121
38	49	50	7
40	8*	14	142
42	70	70	352

H= 8, L= 6

K	FO	FC	ALPHA
2	4*	4	265
4	85	79	211
6	18*	8	304
8	4*	17	344
10	48	53	149
12	13*	13	227
14	4*	24	357
16	60	62	170
18	33	26	153
20	57	60	192
22	43	48	6
24	27*	5	347
26	5*	19	247
28	68	62	21
30	5*	6	170
32	68	59	345
34	21*	17	243
36	21*	29	91

H= 10, L= 6

K	FO	FC	ALPHA
0	112	109	210
2	53	44	164
4	36	19	222
6	69	67	196
8	7*	25	214
10	47	43	92
12	72	74	20
14	25*	20	133
16	60	61	20
18	57	64	23
20	41	36	216
22	21*	16	19

K	FO	FC	ALPHA
H=	10, L=	6	
24	50	44	201
H=	9, L=	7	
1	78	73	167
3	8*	39	18
5	17*	7	238
7	68	71	303
9	50	41	258
11	39	45	227
13	68	63	334
15	5*	19	218
17	39	34	6
19	68	55	118
21	18*	27	88
23	56	62	62
H=	7, L=	7	
1	94	102	239
3	4*	16	331
5	54	55	223
7	28*	17	7
9	58	47	220
11	77	73	123
13	77	76	10
15	28*	25	136
17	35	31	134
19	22*	30	263
21	58	57	233
23	34*	41	298
25	48	67	208
27	36	29	130
29	38	26	212
31	36	21	147
33	55	46	212
H=	5, L=	7	
1	90	83	164
3	79	76	99
5	81	75	211
7	31*	35	92
9	72	66	144
11	78	78	212
13	55	52	135
15	77	79	267
17	54	43	174
19	57	65	104
21	65	70	160
23	49	50	23
25	68	52	117
27	56	44	254
29	10*	21	161
31	54	57	129
33	70	73	343
35	40	47	223
37	41	40	130
39	24*	43	276
H=	3, L=	7	
1	106	113	252
3	116	127	244
5	63	67	147
7	75	75	222
9	30*	28	0
11	70	77	158
13	14*	18	256
15	43	52	255
17	104	115	112
19	75	74	219
21	77	76	169
23	46	47	15
25	35	39	146
27	42	48	279
29	58	65	307
31	65	66	248
33	92	95	350
35	5*	16	205
37	38	38	84
39	38	40	97
41	38	38	152
43	46	64	53
H=	1, L=	7	
1	92	89	246
3	96	96	129
5	160	152	55
7	76	76	129
9	82	89	13
11	56	51	122
13	32	42	235
15	52	53	108
17	97	110	226
19	65	68	306
21	43	37	222
23	62	54	345
25	31*	43	216
27	42	36	88
29	58	67	27
31	94	94	134
33	50	45	24
35	44	39	134
37	37	40	221
39	35	35	135
41	75	71	234
43	43	40	136
45	41	44	190
H=	0, L=	8	
0	260	266	8
4	64	66	274
8	27*	13	232
12	163	158	158
16	85	92	182
20	58	52	350
24	105	106	330
28	103	101	351
32	54	48	173
36	76	83	173
40	70	71	165
H=	2, L=	8	
2	126	114	190
4	55	42	345
6	33*	49	251
8	67	69	349
10	109	96	352
12	4*	7	140
14	107	99	7
16	21*	5	200
18	15*	22	28
20	49	35	181
22	114	116	201
24	4*	9	298
26	71	67	184
28	37	33	343
30	46	48	200
32	5*	23	351
34	102	97	21
36	23*	13	275
38	63	61	19

K	FO	FC	ALPHA
H= 4, L= 8			
0	120	124	27
2	85	98	232
4	45	59	217
6	63	61	215
8	18*	9	15
10	35	38	228
12	62	66	166
14	66	62	16
16	20*	31	134
18	91	86	212
20	4*	21	50
22	48	49	59
24	45	46	336
26	59	48	181
28	46	36	26
30	89	84	202
32	5*	10	161
34	33*	46	228
36	44	37	204
H= 6, L= 8			
2	36	34	243
4	58	58	29
6	21*	14	51
8	64	66	2
10	32*	31	242
12	29*	34	166
14	5*	14	54
16	65	57	155
18	22*	16	250
20	89	87	191
22	5*	11	254
24	8*	7	92
26	24*	18	27
28	52	47	343
30	17*	11	177
H= 8, L= 8			
0	39	50	103
2	60	72	214
4	5*	17	177
6	88	85	189
8	8*	15	136
10	55	57	181
12	49	48	138

K	FO	FC	ALPHA
14	29*	24	4
16	36	28	115
18	75	63	5
20	5*	10	18
H= 7, L= 9			
1	78	87	142
3	28*	7	130
5	35*	21	245
7	27*	6	125
9	34*	29	112
11	68	71	210
H= 5, L= 9			
1	47	45	106
3	5*	28	297
5	27*	5	298
7	61	52	171
9	28*	39	214
11	48	48	141
13	49	52	254
15	37	23	14
17	14*	32	102
19	26*	18	354
21	42	46	194
23	67	74	331
H= 3, L= 9			
1	87	91	146
3	62	56	180
5	16*	25	228
7	48	43	86
9	52	48	217
11	44	49	261
13	37	37	275
15	71	72	297
17	7*	12	295
19	51	58	345
21	39	44	206
23	5*	7	53
25	10*	16	123
27	50	53	89
29	23*	14	61
H= 1, L= 9			

K	FO	FC	ALPHA
1	12*	29	148
3	78	86	280
5	81	72	271
7	87	93	197
9	64	67	305
11	15*	25	177
13	19*	11	94
15	15*	19	15
17	34*	39	82
19	40	44	59
21	59	62	124
23	5*	14	133
25	25*	5	251
27	11*	38	175
29	47	41	110
31	26*	38	224
H= 0, L= 10			
2	91	85	178
6	26*	28	142
10	87	76	3
14	65	57	331
18	11*	17	18
22	42	32	186
H= 2, L= 10			
0	64	55	54
2	25*	34	212
4	44	52	342
6	53	52	174
8	40	38	186
10	32*	35	180
12	63	63	186
14	11*	10	112
16	19*	21	203
18	19*	36	356
20	29*	15	350
H= 4, L= 10			
0	36	0	143
2	22*	22	225
4	44	46	24
6	5*	7	58
8	47	52	353
10	52	46	8
12	18*	28	180

FIGURE 1.

ORTEP DRAWING OF THE CATION $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3]^+$ SHOWING INNER COORDINATION SPHERE WITH MORE RELEVANT BOND DISTANCES AND ANGLES.

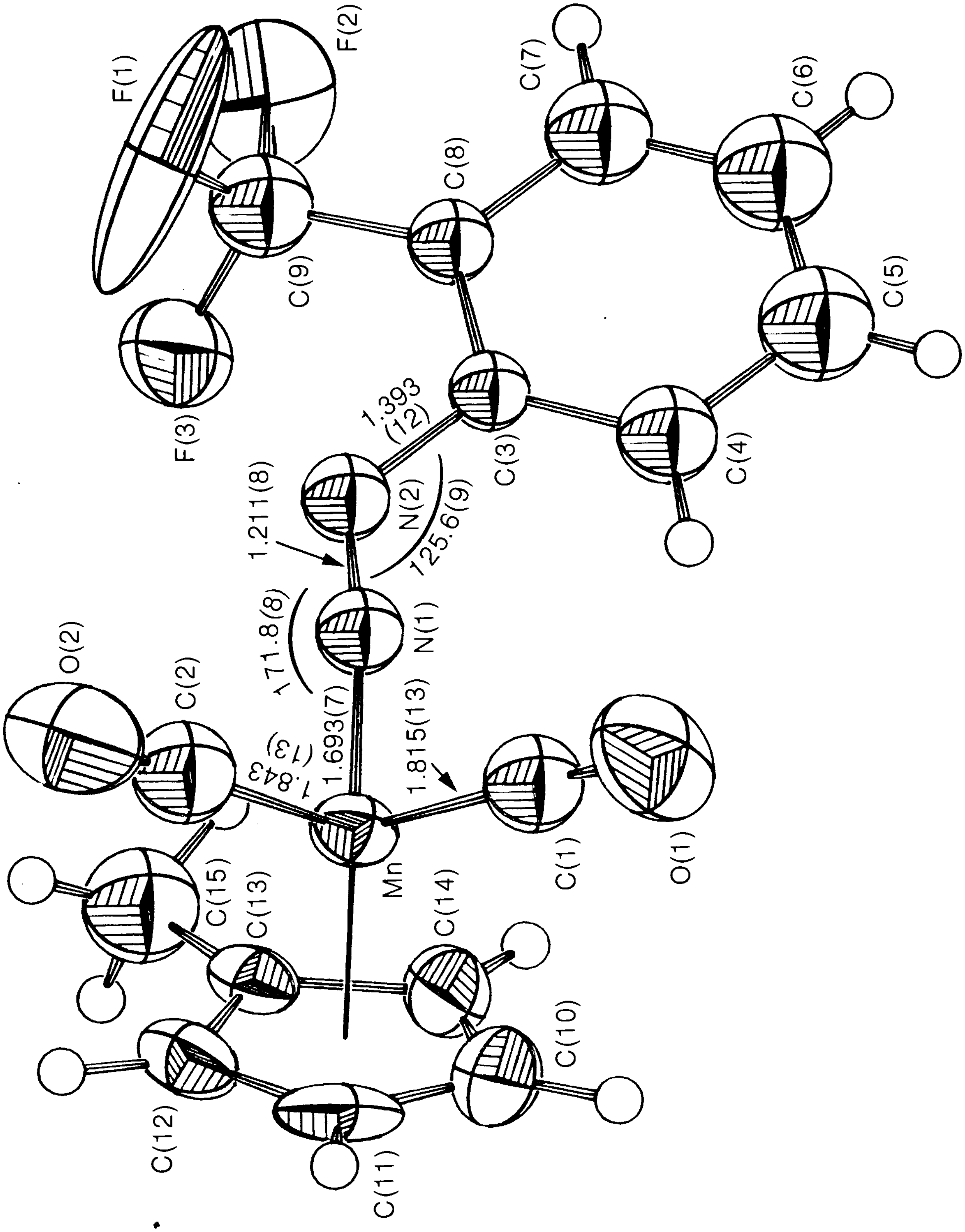

F(1)
F(2)
F(3)
C(9)
C(8)
C(7)
C(6)
C(5)
C(4)
C(3)
N(2)
N(1)
1.393
(12)
1.211(8)
125.6(9)
171.8(8)
1.693(7)
1.843
(13)
1.815(13)
O(2)
C(2)
Mn
C(1)
O(1)
C(15)
C(13)
C(14)
C(10)
C(12)
C(11)

FIGURE 2.

PACKING OF THE UNIT CELL.

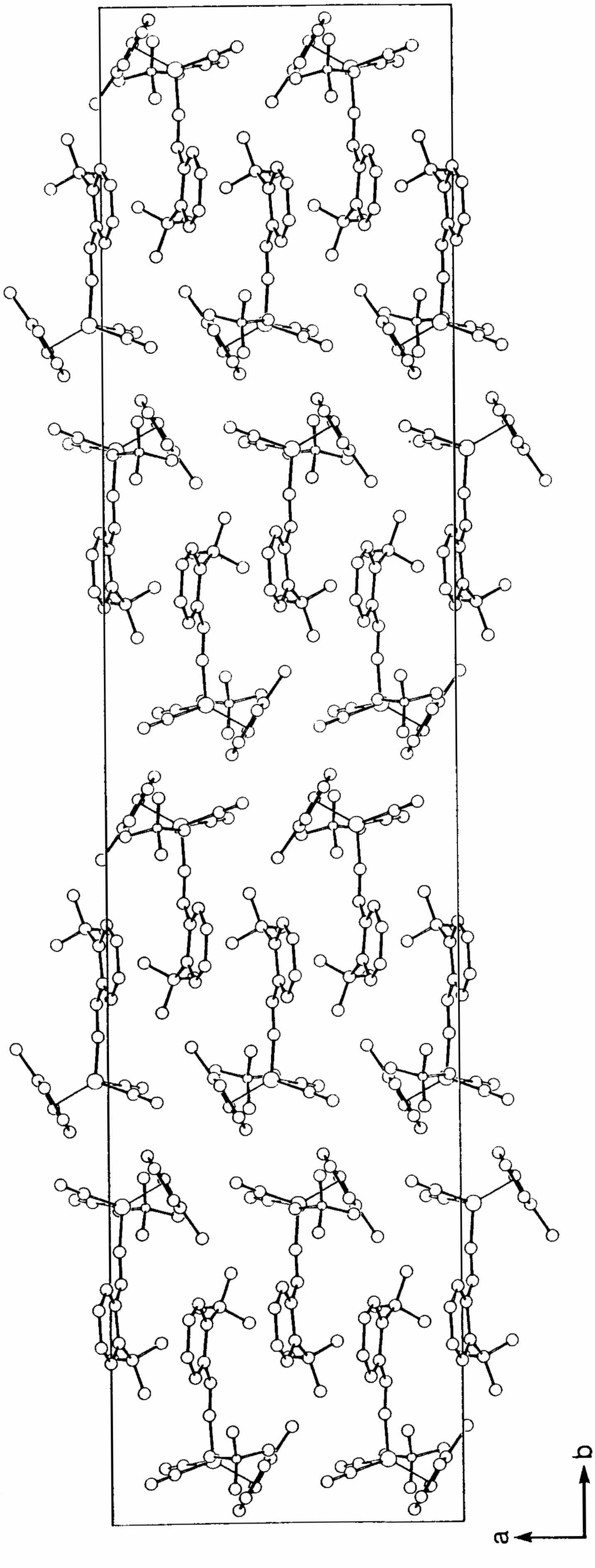
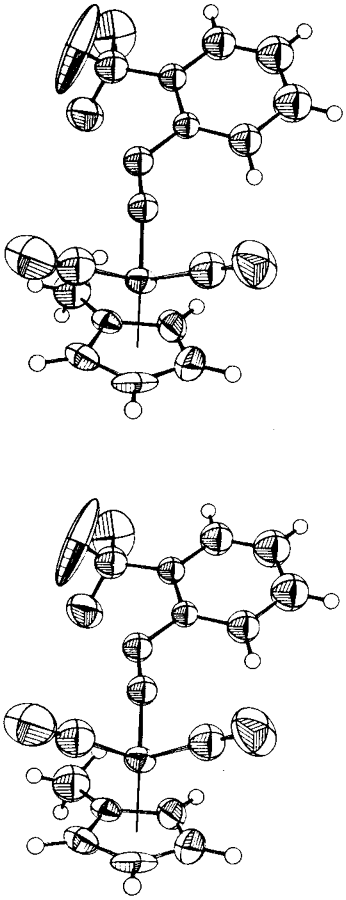

a
b

FIGURE 3

ORTEP STEREODRAWING OF THE MOLECULE

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$



The F-B-F angles range between 108 (2)° and 118 (1)° and the B-F distances range between 1.37 (2) and 1.45 (2) Å.

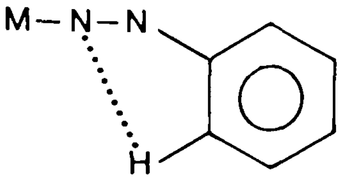
The anion is more or less isolated in the crystal lattice with no significant interactions with atoms surrounding it. The shortest intermolecular contacts involving fluorine atoms are with phenyl and cyclopentadienyl hydrogen atoms, and are in the range 2.42 - 2.81 Å.

The Aryldiazo Ligand

The aryldiazo ligand in this manganese complex assumes the singly-bent geometry, in agreement with the interpretation of the ν(NN) frequency (Chapter 2). The Mn-N(1)-N(2) angle tends towards linearity (171.8(8)°), but the N(1)-N(2)-C(3) angle is bent (125.6(9)°), suggesting approximate sp hybridization about N(1) and sp^2 hybridization about N(2), and a formal structure (2).

The dihedral angles between the least-squares planes of N(1)-N(2)-C(3) and N(2)-C(3)-C(4) (-0.4°) and N(1)-N(2)-C(3) and N(2)-C(3)-C(8) (179°) show the co-planarity of the benzene ring, with N(1)-N(2)-C(3) plane, indicating π-conjunction of the Mn-N-N-Ph network. This has also been found for $[OsH(CO)(N_2Ph)(PPh_3)_2 \cdot CH_2Cl_2]$[7], $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$[6], $[Re(N_2Ph)Cl_2\{P(CH_3)_2Ph\}_3]$[8], $[RuCl_3(\underline{p}\text{-}N_2C_6H_4CH_3)(PPh_3)_2]$[36,51], and $[Mo(N_2Ph)\{S_2CN(CH_3)_2\}_3]$[9].

Possibly, if the planarity of the N(1)-N(2)-Ph group has to be retained for maximized π-conjugation, the angle N(1)-N(2)-C(3) must be greater than the theoretical sp^2 value of 120°, otherwise the N(1).....H(4) contact becomes prohibitively small. (The N(1).....H(4) contact is 2.505(9) Å).



If N(1)-N(2)-C(3) angle is constrained to be 120°, the calculated N(1) .....H(4) distance becomes approximately 2.40 Å, significantly shorter.

Calculations of the equivalent observed N(1)....H distances in previously reported singly-bent aryldiazenido complexes: $[Fe(CO)_2(PPh_3)_2(N_2C_6H_5)][BF_4]^6$, $[OsH(CO)(PPh_3)_2(N_2C_6H_5)]^7$, $[RuCl_3(PPh_3)_2(\underline{p}\text{-}N_2C_6H_4CH_3)]^{36,51}$ and $[Mo(HBpz_3)(CO)_2(N_2C_6H_5)]^5$ were carried out by using the computer program: DANFIG. The results showed that none of these N(1) .....H distances was as short as 2.40 Å. The range found was 2.63 Å for the iron complex to 2.95 Å for the osmium one (see Table 9).

A small difference in the N(1) ....H distance, such as 0.03 Å, produced angles N(1)-N(2)-C(3) significantly different.

The value of the angle N(1)-N(2)-C(3) of 135.9 (11)° in the ruthenium complex, with a N(1) ....H contact of 2.78 Å, cannot permit a good correlation with the other complexes in this series.

The Mn-N(1) distance is 1.693(7) Å, very similar to the corresponding distance observed in the nitrosyl complex $[\eta^5\text{-}CH_3C_5H_4Mn(CO)(NO)(PPh_3)]^{52}$ (1.674(5) Å. This is the shortest metal nitrogen distance found for a singly-bent

TABLE 9

COMPOUND	N(1) ....H Å	N(1)-N(2)-C(3)/°	Ref.
$[RuCl_3(PPh_3)_2(\underline{p}\text{-}N_2C_6H_4CH_3)]$	2.78	135.9(11)	51
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$	2.50	125.6(9)	*
$[Fe(CO)_2(PPh_3)_2(N_2C_6H_5)][BF_4]$	2.63	124.2(6)	6
$[Mo(HBpz_3)(CO)_2(N_2C_6H_5)]$	2.66	121.2(2)	5
$[OsH(CO)(PPh_3)_2(N_2C_6H_5)]$	2.95	118.5(7)	7

* This work

aryldiazenido transition-metal complex (see Table 9) and is comparable with the Fe-N(1) distance found in $[Fe(CO)_2(NNPh)(PPh_3)_2][BF_4]^6$ (1.702(6) Å). This may be attributed to two principal factors: i) the small effective radius of first-row transition metals (1.17 Å covalent radii for Mn and Fe)[53], ii) the positive charge on these complexes.

The N(1)-N(2) distance of 1.211(8) Å is somewhat shorter than the accepted value of 1.24 Å for an N=N double bond[12,13] (from PhN_2Ph). An N≡N triple bond in a free ligand is 1.10 Å (from PhN_2^+)[14].

The N(2)-C(3) distance (1.393(12) Å) is somewhat shorter than a normal N-C single bond (~1.47 Å)[54].

A comparison of bond distances and angles for various transition-metal aryldiazenido complexes is given in Table 10.

All aryldiazo ligands in these complexes have an essentially singly-bent geometry. As the N(1)-N(2)-C(Ph) angle increases there appears to be a decrease in N-N distance, suggesting an increased degree of s-character contribution in the hybridization on the N(2).

TABLE 10

SOME BOND DISTANCES AND ANGLES FOR ARYLDIAZENIDO-TRANSITION METAL COMPLEXES

COMPOUND	M-N/Å	N-N/Å	N-C/Å	M-N-N/°	N-N-C/°	Ref.
$[Mo(S_2CNMe_2)_3(\underline{m}\text{-}N_2C_6H_4NO_2)]$	1.770(6)	1.262(9)	1.410(10)	170.6(6)	117.9(7)	9
$[OsH(CO)(PPh_3)_2(N_2C_6H_5)]$	1.867(6)	1.211(8)	1.460(10)	171.1(6)	118.5(7)	7
$[ReCl_2(PPhMe_2)_3(N_2C_6H_5)]$	1.77 (2)	1.23 (2)	1.43(2)	173 (2)	119 (2)	8
$[Mo(S_2CNMe_2)_3(N_2C_6H_5)]$	1.781(4)	1.233(6)	1.417(7)	171.5(4)	120.5(5)	9
$[Mo(HBpz_3)(CO)_2(N_2C_6H_5)]$	1.825(4)	1.211(6)	1.43 (2)	174.2(1)	121.2(2)	5
$[Fe(CO)_2(PPh_3)_2(N_2C_6H_5)][BF_4]$	1.702(6)	1.201(7)	1.404(8)	179.2(5)	124.2(6)	6
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$	1.693(7)	1.211(8)	1.393(12)	171.8(8)	125.6(9)	(a)
$[RuCl_3(PPh_3)_2(\underline{p}\text{-}N_2C_6H_4CH_3)]\cdot S$	1.784(5)	1.158(6)	1.376(6)	171.9(5)	137.1(5)	36(b)
	1.796(9)	1.144(10)	1.40 (1)	171.2(9)	135.9(11)	51(c)

Abbreviations: Ph: C_6H_5; Me: CH_3; Pz=$C_3H_3N_2$; M=metal; s:solvent

(a) This work; (b) S: CH_2Cl_2; (c)S: acetone

CHAPTER IV

CHEMICAL REACTIONS

Preliminary experimental observations that solutions of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ attacked the KBr and NaCl infrared solution cells, leaving the BF_4 group on the cell walls (shown by the IR spectrum of the cells alone), suggested that this aryldiazenido complex should react with nucleophilic agents.

Indeed, the manganese complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ reacts with a large number of anionic nucleophile agents, such as Cl^-, Br^-, I^-, CN^-, SCN^-, to give the manganese dinitrogen complex $[(\eta^5\text{-}CH_2C_5H_4)Mn(CO)_2N_2]$ (14)

$$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]^+ + X^- \longrightarrow$$

$$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2] + \underline{o}\text{-}XC_6H_4CF_3 \qquad (14)$$

(X = Cl, Br, I, CN, SCN)

This is the first example of synthesis of a dinitrogen complex via an aryldiazenido compound as an intermediate.

These reactions were carried out under very mild conditions (in acetone at room temperature, under one atmosphere pressure of nitrogen), in contrast with previously reported syntheses of the related cyclopentadienyl analogue:

$[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2]$.[24,25] The rate of the reactions seems to follow the trends $I^- > Br^- > Cn^- > SCN^- > Cl^-$.

The manganese-dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ could not be isolated as a pure species. Its pink-red solutions (in acetone or hexane) slowly decomposed at room temperature, even under nitrogen. At -78° C the decomposition process occured much slower. The tricarbonyl $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ was identified among the decomposition products. The other products were not identified.

The dinitrogen complex and o-iodotrifluoromethylbenzene from reaction (14) were characterized by I.R. and especially gas-chromatograph-mass spectroscopy.

The i.r. spectrum of the dinitrogen complex (in acetone) showed two strong carbonyl bands at 1970 and 1911 cm^{-1} and a strong band at 2160 cm^{-1} which was assigned as $\nu(NN)$ by comparison with those values reported for $[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2]$[24,25].

The i.r. spectrum of the o-iodotrifluoromethylbenzene (o-$IC_6H_4CF_3$) was compared with standard I.R. spectra[55] as a way to distinguish among ortho, meta and para isomers.

An unambiguous characterization of these products in solution by GC-mass spectroscopy was carried out. The GC spectrum of this solution showed two major peaks (see Figure 4).

The mass spectrum of the first peak (shorter retention time) with a parent ion at m/e: 272 (Figure 5), corresponds to the o-iodotrifluoromethylbenzene (o-$IC_6H_4CF_3$). The principal ions in this mass-spectrum are shown in Table 11.

FIGURE 4

GC-spectrum of the final solution from reaction (14). Figures 4-A and 4-B correspond to the m/e =272 and m/e =218 ion trace respectively. Figure 4-C, to the GC-spectrum. Peak m/e = 272 : ($\underline{o}$-$IC_6H_4CF_3$)

Peak m/e = 218 : $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$

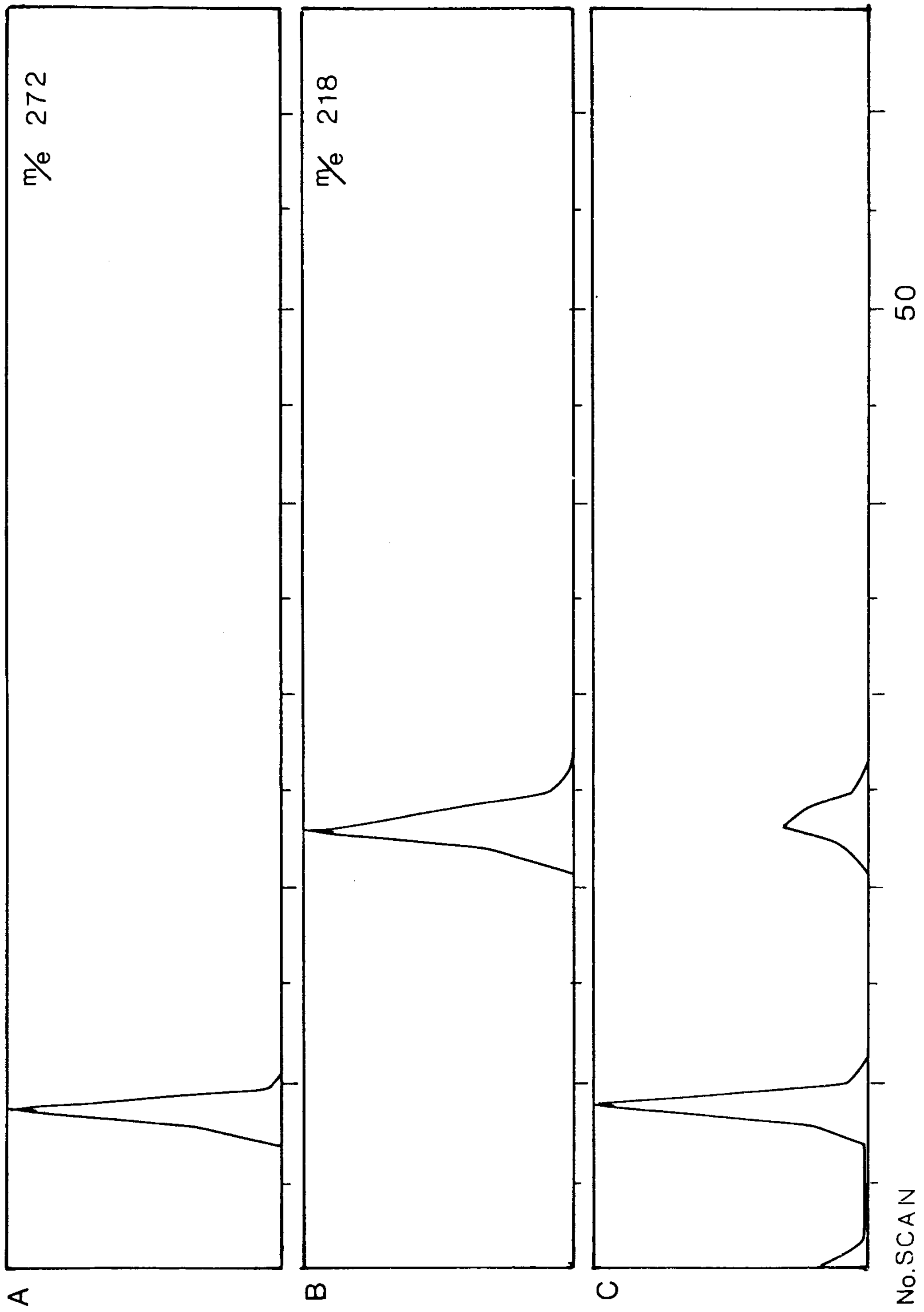

A
B
C
m/e 272
m/e 218
50
No. SCAN

Figure 5

Mass-spectrum of the ortho-$IC_6H_4CF_3$

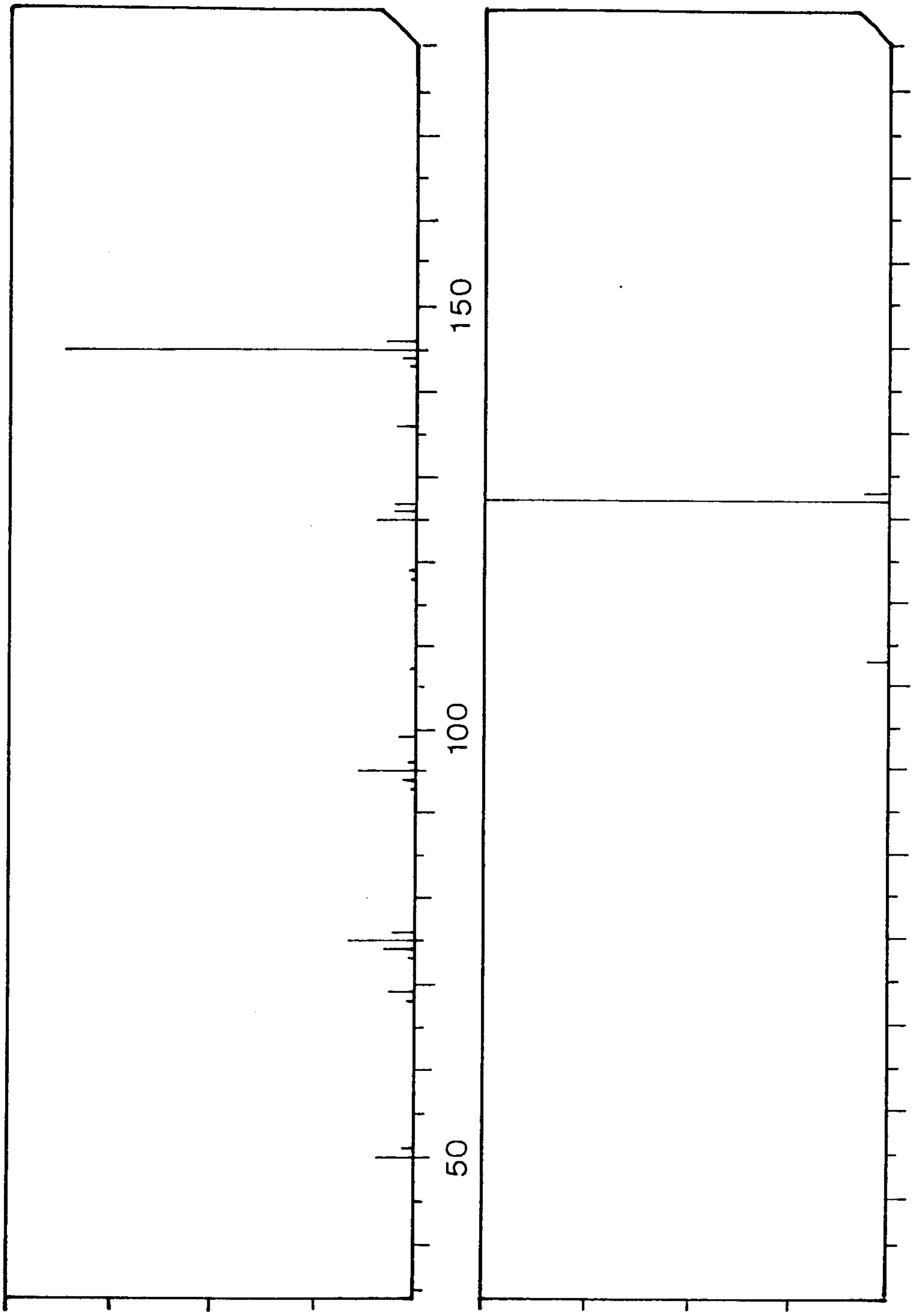

50
100
150
200
250
300

TABLE 11

MASS-SPECTRUM OF ortho-$IC_6H_4CF_3$

m/e	Ions	Relative Abundance
272	$[IC_6H_4CF_3]^+$	100.0
253	$[IC_6H_4CF_2]^+$	5.8
145	$[C_6H_4CF_3]^+$	89.0
126	$[C_6H_4CF_2]^+$	6.2
107	$[C_6H_4CF]^+$	1.6
95	$[C_6H_4F]^+$	25.0
76	$[C_6H_4]^+$	8.1
69	$[CF_3]^+$	10.0
50	$[CF_2]^+$	20.0
127	$[I]^+$	7.8

The mass-spectrum of the second peak (longer retention time) with a parent ion at m/e: 218 (Figure 6) corresponds to the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$. The molecular ion is assumed to first undergo N_z loss from P^+ in view of how easily this ligand is replaced by chemical means in the neutral species, followed by loss of the two CO groups, giving the ion $[(CH_3C_5H_4)Mn]^+$ as the base peak. This principal ions present in this mass-spectrum are shown in Table 12.

Figure 6

Mass-spectrum of the manganese-dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$

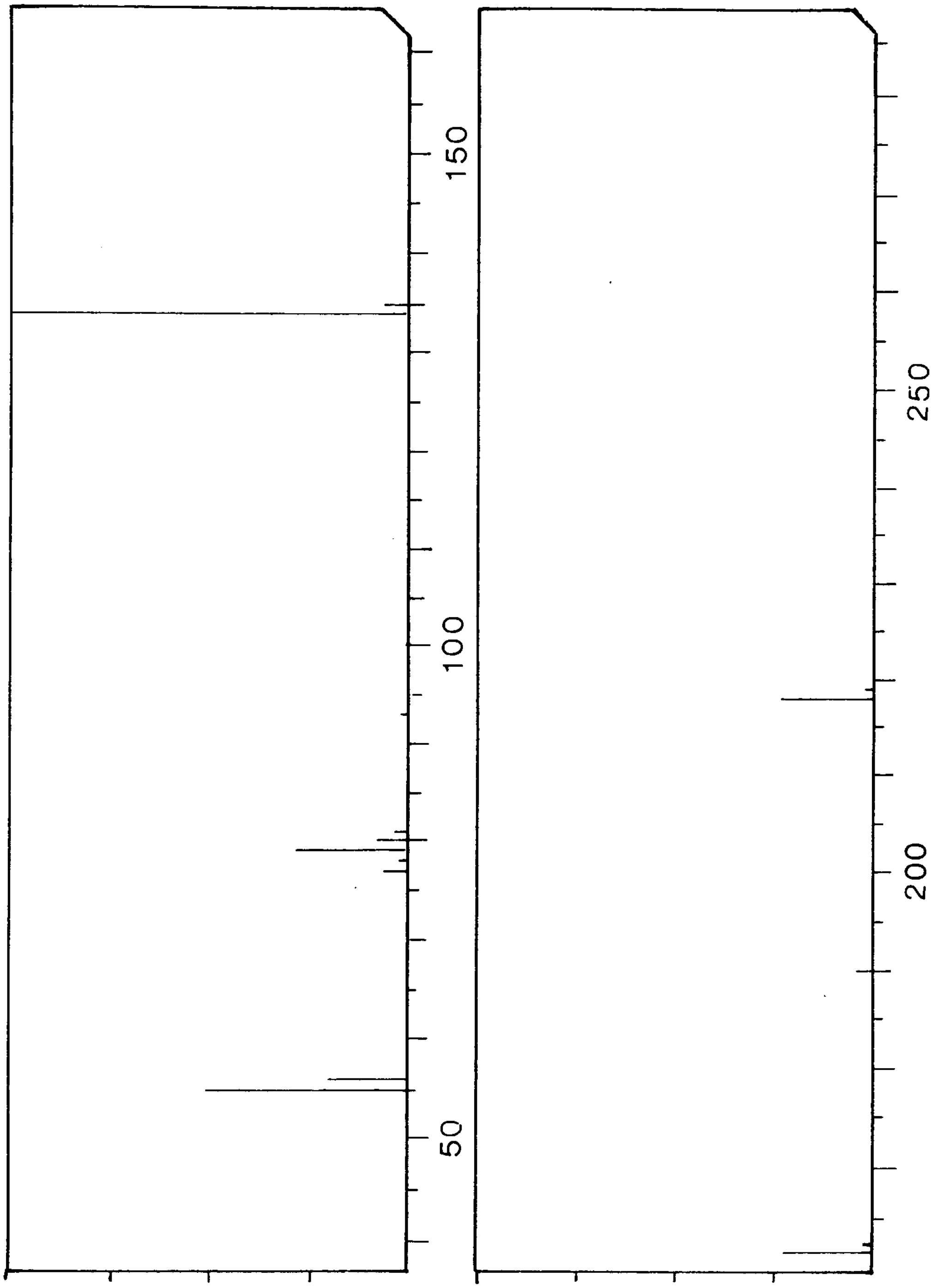

150
100
50
250
200

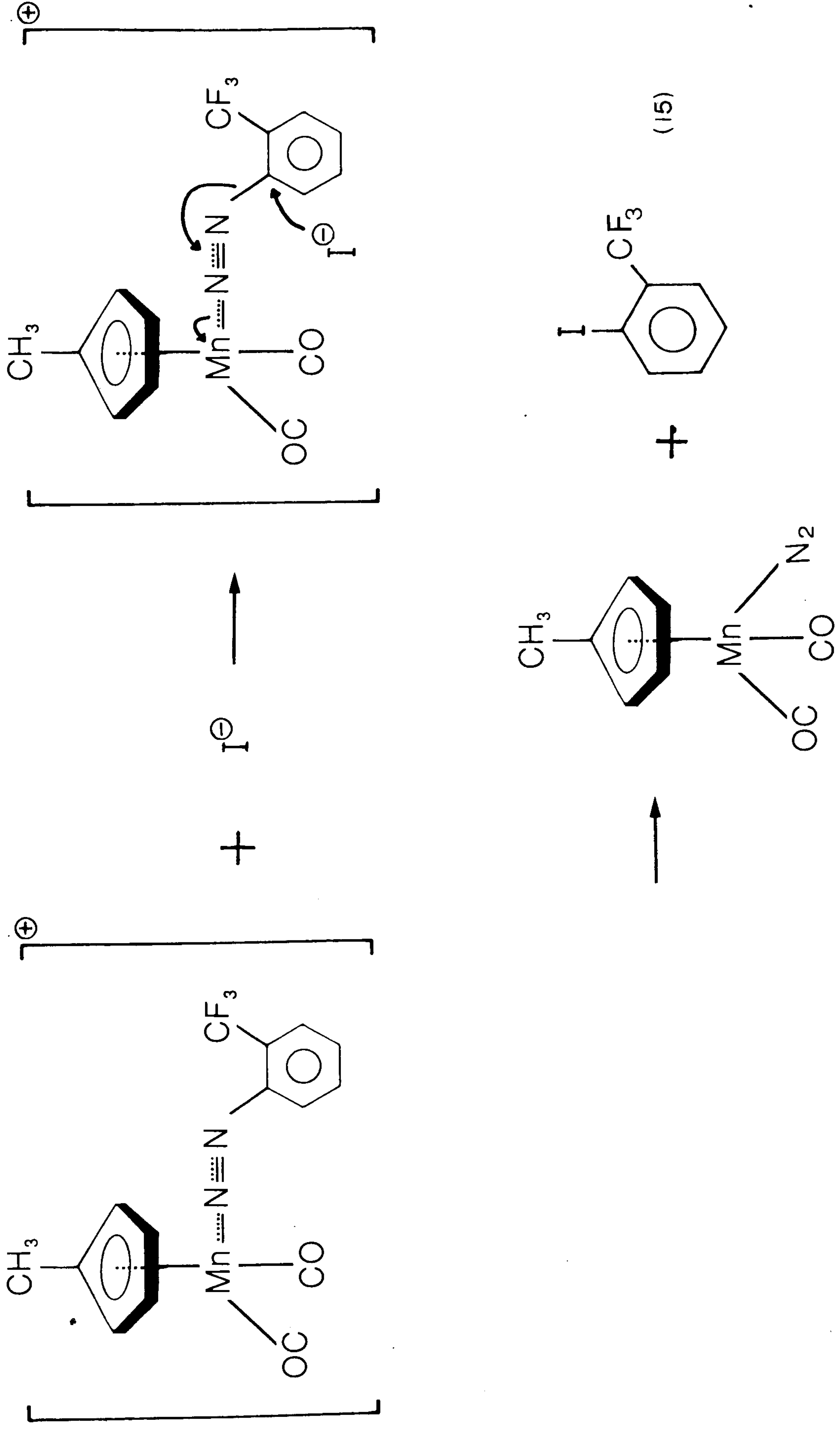
TABLE 12

MASS-SPECTRUM OF $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$

m/e	Ions	Relative Abundance
218	$[(CH_3C_5H_4)Mn(CO)_2N_2]^+$	24
190	$[(CH_3C_5H_4)Mn(CO)_2]^+$	<1
162	$[(CH_3C_5H_4)Mn(CO)]^+$	23
134	$[(CH_3C_5H_4)Mn]^+$	100
79	$[CH_3C_5H_4]^+$	28
56	$[Mn-H]^+$	20
55	$[Mn]^+$	49

Although no kinetic and mechanistic studies were carried out for this reaction, the presence of the o-iodotrifluoromethylbenzene as a final product suggests that a plausible mechanism could be the nucleophilic attack of the iodide (in this case) at the carbon atom of the aryldiazo group bonded to the nitrogen atom N(2) to give the dinitrogen complex (15).

Attacks at the carbon attached to the nitrogen atom in the free diazonium ions by nucleophilic agents, have been reported[71,72].



(15)

A parallel reaction was conducted under an argon atmosphere to establish that the N_2 ligand in the dinitrogen complex came from the aryldiazo group and not from the nitrogen atmosphere. Identical products were indeed obtained, thereby showing that the N_2 ligand originated in the aryldiazo group.

Reaction of the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ with aryldiazonium salts $[\underline{o}\text{-}RC_6H_4N_2][BF_4]$ (R = CF_3, F, H), regenerated the aryldiazenido complexes (16).

$$[(\eta\text{-}CH_3C_5H_4)Mn(CO)_2N_2] + [\underline{o}\text{-}RC_6H_4N_2][BF_4] \longrightarrow$$
$$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4R)][BF_4] + N_2 \qquad (16)$$

This particular reaction is potentially useful for the synthesis of other manganese aryldiazenido complexes which cannot be synthesized by common routes.

Reaction with PPh_3:

Triphenylphosphine (PPh_3), a weak nucleophilic agent, reacts in acetone with the manganese aryldiazenido complex: $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3]^+$ to give the known triphenylphosphine derivative $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$[32] (17).

$$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]^+ + PPh_3 \longrightarrow$$
$$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)] + \text{organic products} \qquad (17)$$

This reaction is not a simple substitution of the aryldiazo group by PPh_3. Following the reaction by I.R. spectroscopy, it was possible to observe the initial formation of the manganese-dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ (ν(CO): 1970, 1911 cm^{-1}) as an intermediate, whose maximum concentration occured at 30 minutes; followed by the appearance in the i.r. spectrum of two new bands in the carbonyl region, which indeed were characterized as the two ν(CO) bands of the triphenylphosphine derivative $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$ (ν(CO): 1938, 1875 cm^{-1}). The bands corresponding to the dinitrogen complex disappeared completely (see Figure 7). The N_2R^+ group was not observed in any of the i.r. spectra.

The dinitrogen complex, as intermediate in this reaction, was separated from the PPh_3 derivative by column-chromatography and was characterized by IR and GC-mass spectroscopy. The triphenylphosphine derivative also was well characterized by elemental analysis, IR, ^{1}H-NMR and mass-spectroscopy. All of these analyses were identical with those obtained from a standard sample of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$ prepared by an alternative method.[32]

When the mixture of PPh_3 and $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]^+$ in acetone was allowed to react until all the aryldiazenido and the dinitrogen complexes (produced during the reaction) were consumed, several products were obtained (from GC-mass spectra of the final solution), most of which were not identified due to the fact that some of them seemed to have decomposed in the GC-column. Only two were characterized: $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ which is from

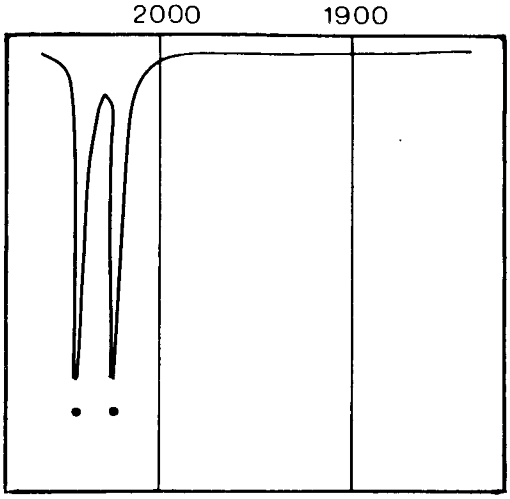
Figure 7

IR-spectra, at different intervals of time, of the reaction between $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3][BF_4]$ and PPh_3. Only the carbonyl region is shown.

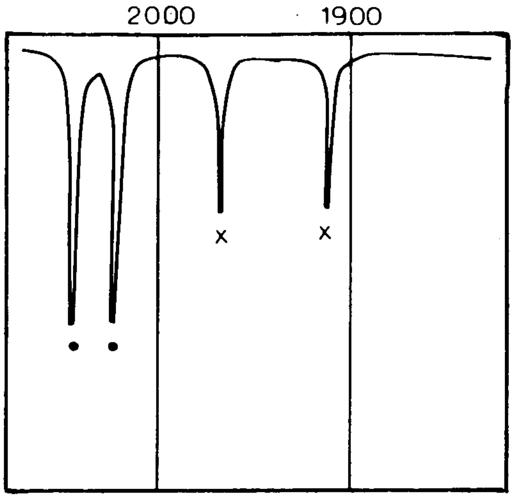
● ν(CO), corresponding to the starting material: $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]^+$

× ν(CO), corresponding to the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$

■ ν(CO) corresponding to the triphenyl phosphine derivative: $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$



TIME: 0 min



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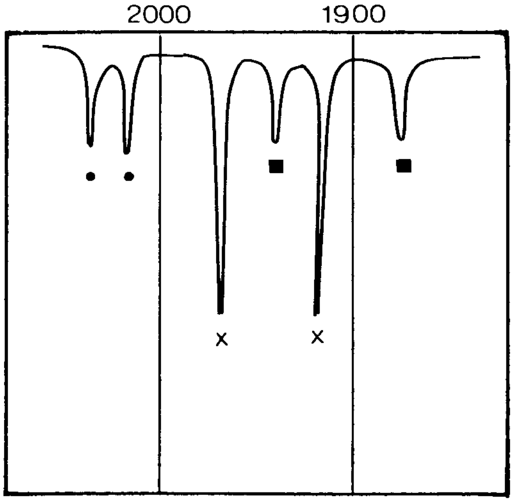

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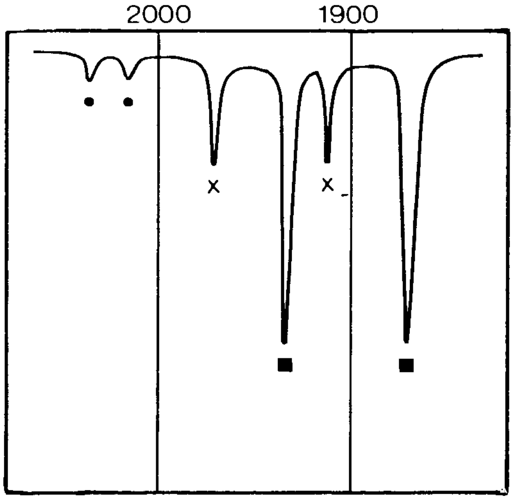
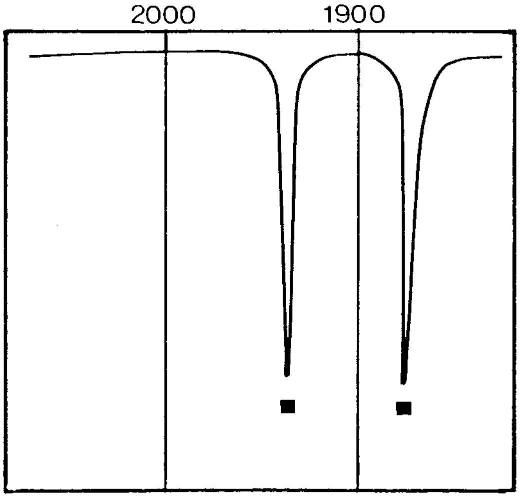


TIME: 160 min



TIME: 360 min

decomposition of the dinitrogen complex; and trifluoromethyl benzene ($C_6H_5CF_3$).

Having observed that the dinitrogen complex $[(\eta^5-CH_3C_5H_4)Mn(CO)_2N_2]$ is an intermediate in this reaction, a mechanism analogous to X^- ($X^- = I^-, Br^-, Cl^-, CN^-, SCN^-$) would result in PPh_3 attack at the carbon atom bonded to the nitrogen atom in the aryldiazo group, with possible formation of the tetraphenyl phosphonium ion $[Ph_3P(\underline{o}-C_6H_4CF_3)]^+$. No evidence of its formation could be found.

To determine whether a tetraphenylphosphonium ion, if formed in this way, could subsequently react with the manganese dinitrogen complex intermediate to give the triphenylphosphine complex observed, a solution of $[(\eta^5-CH_3C_5H_4)Mn(CO)_2N_2]$ was stirred with $Ph_4P^+Br^-$; no triphenyl phosphine derivative $[(\eta^5-CH_3C_5H_4)Mn(CO)_2PPh_3]$ was obtained.

From all these experimental results, it seems that the mechanistic pathway for reaction with PPh_3 is more complicated than is the reaction with X^- nucleophilic agents. The formation of so many compounds, especially the formation of trifluoromethylbenzene, could be accounted for if the mechanism occurs via radicals.

The formation of the dinitrogen-manganese complex by reaction of the aryldiazenido compound with X^- nucleophilic agents, motivated the study of other related transition-metal aryldiazenido complexes, with X^-, in order to determine whether this was a typical reaction for all, or particular singly-bent aryldiazenido compounds. The complexes $[Fe(CO)_2(PPh_3)_2(\underline{o}-N_2C_6H_4R)][BF_4]$; $[Ru(CO)_2(PPh_3)_2(\underline{o}-N_2C_6H_4R)][BF_4]$

and [(η^5-C_5H_5)Mo(CO)$_2$(o-$N_2C_6H_4R$)] (with R = CF_3) were synthesized by reported methods [37,39, 56] (for infrared data see Table 13). The possible effect of a variation in the substituent on the aryldiazo ligand was avoided by preparing only the ortho-CF_3 aryldiazenido derivatives. All of these compounds were allowed to react with iodide or triphenylphosphine, but none of them produced the corresponding dinitrogen complex.

Reaction of [Fe(CO)$_2$(PPh$_3$)$_2$(o-$N_2C_6H_4CF_3$)][BF$_4$] with KI gave the methathesis product [Fe(CO)$_2$(PPh$_3$)$_2$(o-$N_2C_6H_4CF_3$)][I], in agreement with the results found by Fisher and Sutton[37], for the analogous para-bromo derivative, hence there was no special influence of the CF_3 substituent. With triphenylphosphine, no reaction was noted and the starting aryldiazenido compound was recovered.

The complex [Ru(CO)$_2$(PPh$_3$)$_2$(o-$N_2C_6H_4CF_3$)][BF$_4$] did not react with KI in acetone or CH_2Cl_2, but a solution of the complex in acetone reacted with LiI dissolved in methanol, to give the monocarbonyl [RuI(CO)(PPh$_3$)$_2$(o-$N_2C_6H_4CF_3$)]. Haymore and Ibers[56], working with [Ru(CO)$_2$(PPh$_3$)$_2$($N_2C_6H_5$)]$^+$ found that this compound reacted with LiI in acetone/methanol at low temperature, to give principally the six-coordinate complex [RuI(CO)$_2$(PPh$_3$)$_2$($N_2C_6H_5$)] and 10% of the monocarbonyl derivative [RuI(CO)(PPh$_3$)$_2$($N_2C_6H_5$)]. In the present case, the dicarbonyl six-coordinate complex was not obtained, probably because decarbonylation is favored at higher temperatures, so the formation of the monocarbonyl complex was favored under our experimental conditions (22° C). With PPh$_3$, no reaction was observed and, again, the starting aryldiazenido compound was recovered.

The complex $[(C_5H_5)Mo(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]$ did not react with KI in either acetone or pentane. With PPh_3 (in pentane), a CO group was replaced to give $[(C_5H_5)Mo(CO)(PPh_3)(\underline{o}\text{-}N_2C_6H_4CF_3)]$. This compound was characterized by elemental analyses, IR and mass spectrosopy. King and Bisnette[39], working with the para-tolyldiazenido complex, reported similar results with PPh_3, in boiling methylcyclohexane, again, indicating that no different pattern of reactivity results from the presence of the $\underline{o}\text{-}CF_3$ group.

The easier displacement of a carbonyl group by PPh_3 in the $\underline{o}\text{-}CF_3$ derivative (room temperature) than in the para-methyl one (boiling methylcyclohexane), could be accounted for by the strong electron-withdrawing properties of the CF_3 group, which could induce more π-electron back bonding into the aryldiazo ligand attached to the metal atom, implying labilization of the metal-carbonyl bond. The i.r. spectra of these two derivatives showed that the $\nu(CO)$ bands in the $\underline{o}\text{-}CF_3$ complex (2000, 1936 cm^{-1}) appears at higher frequencies than in the para-methyl one (1997, 1925 cm^{-1}), indicative of some labilization of the metal-carbonyl bond in the former complex.

The complex $[(Bpz_4)Mo(CO)_2(\underline{m}\text{-}N_2C_6H_4F)]$[38], also was tested, but it did not react with either iodide or triphenyl phosphine.

Finally, the new complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2(\underline{o}\text{-}N_2C_6H_5CF_3)][BF_4]$, a close rhenium analogue of the manganese aryldiazenido complex, was synthesized and was

TABLE 13

INFRARED DATA OF SOME RELATED ARYLDIAZENIDO COMPLEXES[†]

Compound	ν(CO) cm^{-1}	ν(NN) cm^{-1}
$[Fe(CO)_2(PPh_3)_2(N_2R)][BF_4]$	2039 vs, 1986 vs[a]	1718 vs
	2030 vs, 1983 vs[b]	1715 vs
$[Ru(CO)_2(PPh_3)_2(N_2R)][BF_4]$	2041 vs, 1996 vs[a]	1669s, 1595 m,1570 m
		1540 w
$[(C_5H_5)Mo(CO)_2(N_2R)]$	2000 vs, 1936 vs[c]	1613 vs, 1564 vs
	1998 vs, 1922 vs[d]	*
$[(CH_3C_5H_4)Mn(CO)_2(N_2R)][BF_4]$	2090 vs, 2045 vs[b]	1795 vs
	2083 vs, 2041 vs[d]	1785 br, w
$[(C_5H_5)Re(CO)_2(N_2R)][BF_4]$	2090 vs, 2030 vs[a]	1760 vs
	2082 vs, 2023 vs[a]	*

[†] R □ ortho-$C_6H_4CF_3$; a, dichloromethane; b, $CHCl_3$

C = pentane; d, acetone; * obscured.

allowed to react with KI. A fast reaction took place to give the corresponding known dinitrogen complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2N_2]$. This complex was very well characterized by I.R. and G.C.-mass spectroscopy. The results are in agreement with those reported previously.[57]

All these experimental results have shown that the reaction of aryldiazenido complexes with nucleophilic agents, to produce dinitrogen compounds, evidently is not a general reaction and that there are some factors which are determining whether the reaction takes place or not.

Which factors determine that aryldiazenido complexes will react with nucleophilic agents to give dinitrogen complexes? The absolute answer is still unknown, but by analyzing the infrared data in Table 13, it seems that the principal ones may be the positive charge on the complex and the nature of the other ligands bonded to the same metal atom. Thus, the positive charge on the complexes decreases the electrondensity on the metal, producing a decrease of back bonding to the carbonyl groups and the aryldiazo ligands, so that the stretching modes of CO and NN appear at high frequency values.

The isoelectronic and isostructural manganese and rhenium ionic complexes, which incidentally show the highest values of $\nu(NN)$ of the compounds studied, were the ones which reacted with X^- nucleophilic agents to give the corresponding dinitrogen complexes.

The iron and ruthenium complexes did not produce a dinitrogen compound, probably due to the presence of the triphenylphosphine ligands, which are strong donor ligands, increasing the electron density on the metal, which could be transmitted to the carbonyl and aryldiazo ligands as electron density back donation. This is supported by the infrared values of the ν(CO) and ν(NN) modes.

The molybdenum complex is a neutral complex and presents the lowest value of CO and N-N stretching in the series. As expected, it did not produce the corresponding dinitrogen compound by reaction with X^- nucleophiles.

Possibilities for this reaction occurring in other aryldiazenido compounds seem to be good for 18-electron cationic complexes possessing a ν(NN) frequency value higher than the value found in the iron complex $[Fe(CO)_2(PPh_3)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]^+$ (ν(NN) = 1718 cm^{-1}).

Reaction of nucleophilic agents X^- with two singly-bent aryldiazenido complexes (with high ν(NN) frequency values): $[RuCl(bipy)_2(\underline{p}\text{-}N_2C_6H_4OCH_3)][PF_6]_2$[66] (ν(NN) = 2095 cm^{-1}) and $[IrCl(PPh_3)_2(N_2C_6H_5)][PF_6]$[65] (ν(NN) = 1868 cm^{-1}), have been reported. Neither reaction produced the corresponding dinitrogen complexes.

The dipositive ionic ruthenium complex was reported[66] to react with excess of KI to give $[Ru(bipy)_2I_2]$, p-iodoanisole ($\underline{p}\text{-}IC_6H_4OCH_3$) and N_2 gas. This reaction was carried out at 60° C. The presence, especially of the p-iodoanisole and N_2 gas, suggests that reaction is occuring by the attack of I^-

at the carbon atom bonded to the nitrogen atom in the aryldiazo group, as in the manganese complex, and that, if the same reaction is carried out at lower temperatures, there is a good possibility of observing the corresponding dinitrogen complex $[RuCl(bipy)_2N_2]^+$.

The iridium complex, however, was reported[65] to react with 1 equivalent of LiCl to give the complex $[IrCl_2(PPh_3)_2(N_2C_6H_5)]$, and in the presence of excess Cl^- or $CHCl_3$ to give $[IrCl_3(PPh_3)_2(N_2HC_6H_4)]$. Also this compound reacted with carbon monoxide, isonitriles, phosphines, arsines and stibines to form the respective five-coordinate species. With five-coordination occurs a sharp decrease in ν(NN) by about 200 cm^{-1} for PR_3, AsR_3 and SbR_3 and 350 cm^{-1} for CO and RNC.

All these results suggest that the complex $[IrCl(PPh_3)_2(N_2C_6H_5)]^+$ did not produce the corresponding dinitrogen compound, probably because it is a coordinatively unsaturated 16-electron complex and the nucleophilic ligands really added preferentially into the coordination sphere of the metal, to give 18-electron complexes, instead of attacking the aryldiazo group to produce the dinitrogen compound.

At this point, further work should be carried out to test other aryldiazenido complexes possessing high ν(NN) frequency values, ligands other than cyclopentadienyl, and similar metals, to clarify the real importance of those two factors discussed above.

EXPERIMENTAL

GC-Mass spectra were obtained by use of a Hewlett Packard 5985 GC/MS system (70 eV).

a.) Methyl-cyclopentadienyl dinitrogen dicarbonyl manganese: $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$

To 100 mg of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ dissolved in 10 ml of dry acetone, a stoichiometric quantity of KX (X = I, Br, Cl, SCN, CN) as a solid was added (ratio 1:1) and was stirred at room temperature. The course of the reaction was followed by I.R. When all of the starting material was consumed, 10 ml of hexane was added, precipitating a solid which was identified as KBF_4. Filtration gave a clear pink-red solution. This was cooled to -78° C to give two solvent layers, the red bottom layer (acetone) being very concentrated in the dinitrogen complex and $\underline{o}\text{-}C_6H_4CF_3I$. This was the solution used to get the GC-mass spectrum.

I.R. spectrum (acetone): $\nu(CO)$: 1970 vs, 1911 vs cm^{-1}

$\nu(N{\equiv}N)$: 2160 vs.

The iodotrifluoro methylbenzene $(IC_6H_4CF_3)$ was identified to be ortho by comparison of its i.r. spectrum with the standard i.r. spectra[55] of the ortho, meta and para isomers; essentially the assignment was based on the bands at 1595, 1579, 1313, 1265 cm^{-1} and those in the region 800-600 cm^{-1} in the ortho-isomer which are shifted, absent, or of different relative intensities in the other two isomers.

Note: In similar further reactions, an excess of KX salts was used instead a ratio 1:1 with no change in the nature of the reaction, but their completion was faster.

Solutions of the dinitrogen complex were air sensitive, and decomposed slowly at room-temperature even under nitrogen. Low temperatures produced much slower decomposition.

b.) Reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ with PPh_3

The complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ (102 mg; 0.226 mmol) was dissolved in 10 ml of dry acetone and 59 mg (0.226 mmol) of solid PPh_3 was added and stirred at room temperature for 6 hr. The color of the solution changed from deep red to yellow. The solution was concentrated under vacuum to about 2 ml and hexane was added. Yellow crystals of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$ were obtained after leaving the solution in the freezer at -12° C. Also, this complex can be precipitated out very easily by addition of water.

I.R. spectrum (acetone): $\nu(CO)$: 1938 vs, 1875 vs cm^{-1}.

During this reaction, the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ as an intermediate was observed. The isolation of this complex from the starting manganese complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ and the final product $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2PPh_3]$ was carried out in the following way: the reaction was done in 2 ml of dry acetone; after 30 min of stirring (time where the maximum concentration of the dinitrogen complex was obtained), it was passed through a cellulose chromatography column (Sigmacell) prepared in benzene. The column was eluted with benzene and an orange-yellow fraction was collected. The IR-spectrum of this fraction showed the presence of the dinitrogen complex and the final triphenylphosphine derivative.

This fraction was passed through a second chromatography column (silica-gel in benzene) and eluted with benzene. The eluate contained only the complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2PPh_3]$. The dinitrogen complex remained, as a red-orange band, on the top of the column. This complex was removed from the column by elution with acetone.

c.) Methyl-cyclopentadienyl triphenylphosphine dicarbonyl manganese $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2PPh_3]$

This compound was prepared by the photochemical reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ with PPh_3 as described elsewhere.[32]

A mixture of 8 ml of $CH_3C_5H_4Mn(CO)_3$ (0.0512 mol) and 13.4 g of PPh_3 in 150 ml of hexane was irradiated for 3 h. No decomposition was noted. Yellow crystals precipitated out of the solution in 80% yield and were washed with cool hexane to remove the unreacted tricarbonyl. No further purification of the crystals was necessary.

Analysis: Calculated for $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2PPh_3]$

C, 69.04; H, 4.87

Found: C, 69.17; H, 4.90

IR-spectrum (acetone): ν(CO): 1938 vs, 1875 vs cm^{-1}

The ^1H-NMR-spectrum in acetone-d_6 using TMS as internal standard showed peaks in ppm at 1.91 (singlet, CH_3); 4.12 (multiplet); 4.27 (multiplet); protons of the cyclopentadienyl ring and at 7.41 (multiplet, phenyl hydrogen atoms of the PPh_3 ligand), with relative intensities of 3,2,2,15 respectively.

d.) Reaction of the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ with $Ph_4P^+Br^-$

A solution of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ in acetone was stirred with $Ph_4P^+Br^-$ at room temperature for 3 h. The reaction mixture was filtered. IR and GC-mass spectral of this solution did not show any new product. No reaction occurred. Only tricarbonyl $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ from partial decomposition of the dinitrogen complex was noted.

e.) Reaction of $[Ru(CO)_2(PPh_3)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ with LiI

To 100 mg of $[Ru(CO)_2(PPh_3)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ dissolved in 10 ml of dry acetone, a stoichiometric quantity of LiI dissolved in 1 ml of methanol was added and stirred for 15 min at room-temperature. When LiI was added, instantaneously the color of the solution changed from yellow to green and, finally, to orange. An orange solid precipitated out of the solution: $[RuI(CO)(PPh_3)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]$.

The IR-spectrum of this solid as a mujol mull, showed only one carbonyl band at 1912 vs; two weak bands at 1605 and 1550 cm^{-1} which probably are associated with ν(NN). Also, the spectrum showed one band at 1310 cm^{-1} which corresponds to the CF_3 group on the aryldiazo ligand.

f.) Reaction of $[(C_5H_5)Mo(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]$ with PPh_3

A mixture of 100 mg (0.25 mmol) of $[(C_5H_5)Mo(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]$, 69 mg (0.26 mmol) of PPh_3 and 10 ml of pentane was stirred for 2 h. at room temperature. An orange-brown microcrystalline solid precipitated out of the solution, which was characterized as $[(C_5H_5Mo(CO)(PPh_3)(\underline{o}\text{-}N_2C_6H_4CF_3)]$

Analysis: Calculated for $[(C_5H_5)Mo(CO)(PPh_3)(\underline{o}\text{-}N_2C_6H_4CF_3)]$

	C, 59.24;	H, 3.82;	N, 4.46
Found:	C, 59.12;	H, 3.95;	N, 4.39

IR-spectrum in nujol mull showed a single CO band at 1880 vs cm^{-1}. Also showed the band corresponding to the CF_3 group at 1316 s cm^{-1}.

Mass spectrum of this compound under chemical ionization conditions showed the molecular peak as a mixture of M and (M + 1) with the seven natural isotopes of the molybdenum.

M: 624 and (M + 1):625 (MW = 624)

g.) Hydrido triphenylsilyl (η^5-cyclopentadienyl) dicarbonyl Rhenium: $[(\eta^5\text{-}C_5H_5)ReH(CO)_2SiPh_3]$[58]

Commercial $Re_2(CO)_{10}$ (Strem Chemicals, Inc., Newburyport, MA) was converted to $Re(CO)_5Br$ in 99% yield by reaction with 1:1 equivalent of bromine in dichloromethane solution at 0° C[59]. The $Re(CO)_5Br$ was then converted to $(C_5H_5)Re(CO)_3$ in 90% yield by treatment with 1:1 equivalent of thallium cyclopentadienide[60] in boiling redistilled tetrahydrofuran for 16 h. The $C_5H_5Re(CO)_3$ was recrystallized once from a mixture of dichloromethane and hexane before use.

A solution of $(C_5H_5)Re(CO)_3$ (1.7 g, 5.2 mmol) and $HSiPh_3$ (4.0 g, 15 mmol) in 150 ml of cyclohexane was irradiated with a 200 watt source for 20 h. The reaction mixture was suction filtered through a silicic acid column (compound absorbed on column). Eluation with 300 ml of hexane removed all the triphenylsilane unreacted. Then the column was eluated with 150 ml of 30% dichloromethane-hexane. This eluate contained $(C_5H_5)Re(CO)_3$. Then eluation with dichloromethane afforded the product and a small amount of $(C_5H_5)Re(CO)_3$. Sublimation of the crude product at 60° removed the tricarbonyl; crystalization of the unsublimed solid from CH_2Cl_2/hexane afforded white crystals of $(C_5H_5)ReH(CO)_2SiPh_3$ (0.25 g, 9%).

IR-spectrum (in cyclohexane): $\nu(CO)$: 1999 vs and 1932 vs cm^{-1}.

h.) Synthesis of $[(\eta^5\text{-}C_5H_5)Re(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$

To 55 mg of $(\eta^5\text{-}C_5H_5)ReH(CO)_2SiPh_3$ dissolved in 10 ml of dry acetone, an excess of $[\underline{o}\text{-}N_2C_6H_4CF_3][BF_4]$ as solid was added and stirred for 3 h at 65° C. The solution took a deep red-brownish color. The solution was concentrated under vacuum to about 2 ml and diethyl-ether was added until most of the unreacted diazonium salt precipitated. To the filtrate, toluene was added and it was left overnight at -78° C. An orange air-stable microcrystalline solid precipitated out of the solution in yield = ~30%.

Analyses: Calculated for $[(\eta^5\text{-}C_5H_5)Re(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$

	C, 29.63;	H, 1.59;	N, 4.94
Found:	C, 29.60;	H, 1.63;	N, 4.84

I.R.-spectra: (acetone): $\nu(CO) = 2082$ vs, 2023 vs cm^{-1}

(CH_2Cl_2) : $\nu(CO) = 2090$ vs, 2030 vs cm^{-1}

$\nu(NN) = 1760$ vs cm^{-1}

i.) Cyclopentadienyl dicarbonyl dinitrogen rhenium $[(\eta^5\text{-}C_5H_5)Re(CO)_2N_2]$.

This complex was prepared in a similar way to the corresponding manganese dinitrogen complex, by reaction of the aryldiazenido rhenium compound with iodide.

To 30 mg of $[(\eta^5\text{-}C_5H_5)Re(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)][BF_4]$ dissolved in 10 ml of dry acetone, a stoichiometric quantity (or excess) of KI as a solid was added and stirred at room temperature. An i.r. spectrum of the solution after 5 min. of the addition of KI, showed the presence of the dinitrogen complex and very little of the starting aryldiazenido compound.

After 30 min., the solution was pumped to dryness. The dinitrogen complex was sublimed as pale yellow crystals from the residue under high vacuum at 20° C.

I.R. - (in acetone): $\nu(CO) = 1960$ vs, 1898 vs cm^{-1}

$\nu(N{\equiv}N) = 2142$ vs cm^{-1}

MS. The mass spectrum of this complex showed the parent peak with the two natural isotopes of the rhenium ($M^+ = 334$, 336) (17, 27%)

Other peaks:

m/e	ion	relative abundance
306, 308	$C_5H_5Re(CO)_2^+$	24, 38%
278, 280	$C_5H_5Re(CO)^+$	43, 65%
250, 252	$C_5H_5Re^+$	59, 100%
185, 187	Re^+	16, 24%

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