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TRANSITION METAL HYDRIDES
OF THE
IRON NITROSYL GROUP

BY

ALAIN FORGUES, B.Sc.

A thesis submitted to the School of Graduate Studies
in partial fulfillment of the requirements for
the degree of
Master of Science
in the
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University of Ottawa
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ABSTRACT

In chapter I, the protonation of the anion $Fe(CO)_3NO^-,Na^+$ is described. Addition of trifluoroacetic acid on $Fe(CO)_3NO^-,Na^+$ in ether in the presence of six equivalents of triphenylphosphine yielded the disubstituted hydride $HFe(CO)(NO)(P(C_6H_5)_3)_2$, having a reasonable kinetic stability at 25°C. Its structure was established by NMR, IR, elemental analysis and finally by a single crystal X-ray study. It was successfully demonstrated that the reaction proceeded through the monosubstituted iron nitrosyl intermediate $HFe(CO)_2(NO)(P(C_6H_5)_3)$. Unlike $HFe(CO)(NO)(P(C_6H_5)_3)_2$ which is air stable for weeks in the solid state, $HFe(CO)_2(NO)(P(C_6H_5)_3)$ instantaneously oxidized to a mixture of degradation products $(P(C_6H_5)_3)Fe(CO)(NO)_2$, $(P(C_6H_5)_3)Fe(CO)_4$, $(P(C_6H_5)_3)_2Fe(CO)_3$, $(P(C_6H_5)_3)_2Fe(NO)_2$. Comparing the reactivity of the new iron nitrosyl hydrides to that of the isoelectronic cobalt hydrides ($HCo(CO)_x(P(C_6H_5)_3)_y$; $x+y=4$) towards substitution, it was shown that the NO ligand induces a greater accessibility to the coordination sphere of the metal.

This was demonstrated in the reaction of the hydride $HFe(CO)_2(NO)(P(C_6H_5)_3)$ with an excess of $P(C_6H_5)_3$ which yielded the disubstituted hydride $HFe(CO)(NO)(P(C_6H_5)_3)_2$, unlike $HCo(CO)_3(P(C_6H_5)_3)$ which is inert towards further CO substitution with $P(C_6H_5)_3$.

These iron nitrosyl hydrides thermally decomposed to give monometallic degradation products ($Fe(CO)_x(P(C_6H_5)_3)_y$ $x+y=5$; $Fe(NO)_2(CO)_x(P(C_6H_5)_3)_y$ $x+y=2$) resulting from ligand exchange. For such an exchange reaction to occur, the formation of a dimer appears to be a prerequisite. Hence it can be concluded that iron nitrosyl metallic dimers are unstable with respect to ligand redistribution and fragmentation into new monometallic compounds. When compared to cobalt carbonyl hydrides, this is the most striking difference. These cobalt hydrides are known to decompose into metallic dimers which are not subject to further facile decomposition to monometallic products.

Depending on the conditions used (THF instead of ether; HBF_4 instead of CF_3COOH), protonation of the anion $Fe(CO)_3NO^-,Na^+$ also yielded the cation $[Fe(CO)_2(NO)(P(C_6H_5)_3)_2]^+BF_4^-$. Formation of the hydride $HFe(CO)_2(NO)(P(C_6H_5)_3)$ was detected through IR monitoring of the reaction mixture. In this reaction, the dihydride $[H_2Fe(CO)_2(NO)(P(C_6H_5)_3)]^+$ could be also a logical intermediate.

Substitution of a CO with $P(C_6H_5)_3$ was expected to increase the basicity of the metal and consequently enhanced the stability of a cationic iron nitrosyl dihydride with respect to H_2 elimination. This led us to study in chapter II, the protonation of the hydride $HFe(CO)(NO)(P(C_6H_5)_3)_2$. Instead of the generation of the expected dihydride, the reaction proceeded towards the rapid formation of the "pseudo coordinatively" unsaturated cation $[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ with concurrent H_2 loss. All available results suggested the presence of a very accessible coordination site. For example under approximately one atmosphere of CO, $[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ underwent a clean solid-gas reaction to form the coordinatively saturated cation $[Fe(CO)_2(NO)(P(C_6H_5)_3)_2]^+BF_4^-$. Also on dissolving $[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ in methylene chloride or acetone, decomposition into $Fe(NO)_2(P(C_6H_5)_3)_2$ resulted. However, on dissolution of $[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ in acetonitrile, the acetonitrile complex $[Fe(CO)(NO)(P(C_6H_5)_3)_2(CH_3CN)]^+BF_4^-$ was formed which was soluble without any decomposition in chlorinated solvents and acetone. The coordinated acetonitrile showed a very high lability.

Finally in chapter III, the reduction of the iron nitrosyl cation $[Fe(CO)_2(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ with hydride transfering reagents, was studied. Addition of one to three equivalents of reducing agent on the cation $[Fe(CO)_2(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ resulted in the decomposition products $Fe(NO)_2(P(C_6H_5)_3)_2$, $Fe(CO)_4(P(C_6H_5)_3)$ and a small quantity of $Fe(CO)_3(P(C_6H_5)_3)_2$. The course of the reaction was drastically altered when an excess of the reducing agent (6 equivalents) was used. The anion $(P(C_6H_5)_3)Fe(CO)_2(NO)^-,Li^+$ was generated exclusively. In an attempt to identify at least one of the primary processes implicated in the formation of this anion, the reduction was done directly in the NMR tube at low temperature by mixing the cation $[Fe(CO)_2(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ with a limited quantity of the reducing agent. The ^1H NMR showed conclusively the formation of the formyl complex $(P(C_6H_5)_3)_2(NO)(CO)FeCHO$. Preparation of the anion $(P(C_6H_5)_3)_2Fe(CO)(NO)^-,Li^+$ and its reaction with CO to give $(P(C_6H_5)_3)_2Fe(CO)_2(NO)^-,Li^+$ is also discussed.

The ion pairing phenomena observed for the iron carbonyl nitrosyl anions, synthesized during this work, are discussed in the appendix.

GENERAL INTRODUCTION

It was in the early 1930's with the discovery by Hieber of the unstable hydridocarbonyls, $H_2Fe(CO)_4$ (1) and $HCo(CO)_4$ (2) that hydride complexes of the transition metals became and remained a laboratory curiosity for a relatively long period of time. Three additional examples of hydride complexes were reported in 1955, namely $HRe(C_5H_5)_2$ (3), $HCr(C_5H_5)(CO)_3$ and $HMo(C_5H_5)(CO)_3$ (4). However, it was not until two years later after the discovery of trans-$HPtCl(P(C_2H_5)_3)_2$ by Chatt, Duncanson and Shaw (5) that advances in the syntheses of hydride complexes have been especially significant. Since then hydride complexes, containing such diverse ligands or groups as tertiary phosphines, amines, nitrogen, carbonyls etc. have been isolated and characterized for most of the transition metals (6, 45, 47).

Recent years have seen a tremendous growth of research activity in the field of these very important class of compounds (44, 45, 46). Some have found their application in organic and organometallic synthesis (7, 34, 44, 45). The pivotal role of others have been recognized in many catalytic reactions such as hydrogenation (48, 49, 50), isomerisation or hydroformylation of olefins (7, 54) and also in the methanolysis of CO (110). $HCo(CO)_4$, one of the most extensively studied hydride so far is catalytically active in all of these reactions (7, 34, 110).

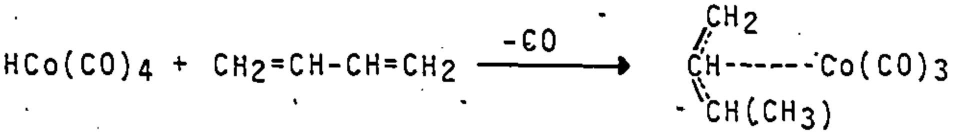
It is noteworthy to indicate that the cobalt catalyzed hydroformylation of olefins was discovered as a side reaction of the Fisher-Tropsch reaction (H_2 reduction of CO to synthetic fuel) catalyzed by an heterogeneous cobalt catalysts (76). For that particular reaction, involved in several practical applications, iron based catalysts are also active and are currently used in Sasol (South Africa) mainly for economical reasons. It is most likely that transition metal hydrides are also implicated as reaction intermediates in the Fischer-Tropsch reaction (34). Provided the mechanisms (which are still very speculative (34) for both the iron and cobalt based catalysts) are similar (190) in these Fischer-Tropsch reactions, that could suggest the occurrence of a class of iron hydrides whose reactivity might parallel to a certain extent those of selected cobalt hydrides such as $HCo(CO)_4$.

The search for these iron hydrides should be worthwile to pursue in an effort to develop ultimately new catalysts for reactions implicating synthesis gas.

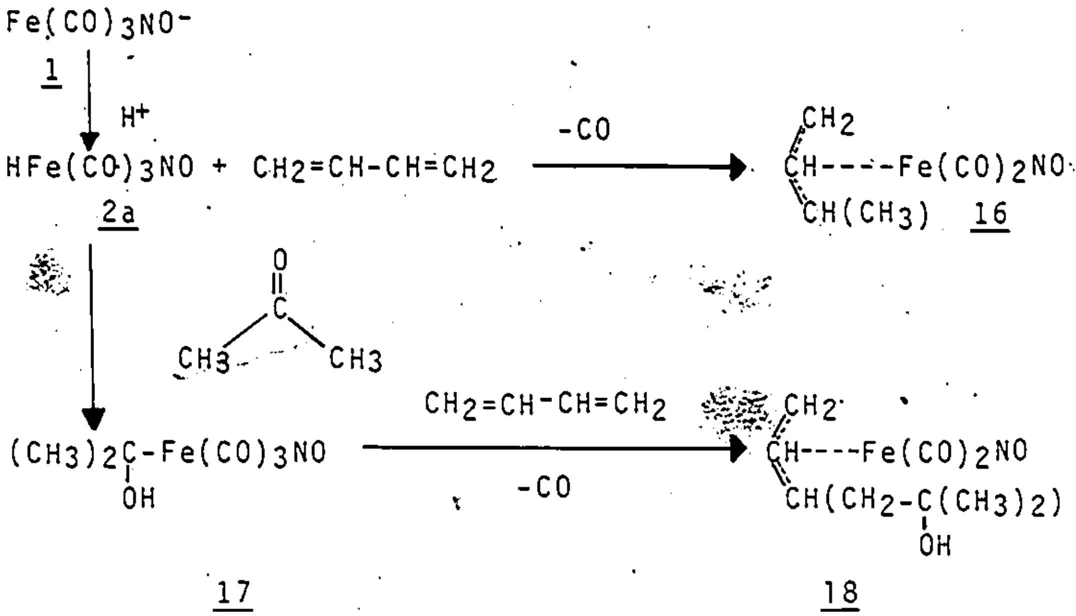
In that context, carbonyl hydrides containing a nitrosyl ligand attracted our interest. While investigating the use of the iron nitrosyl anion $Fe(CO)_3NO^-,Na^+$ as a reagent for organic synthesis (42, 43), it appeared to us that there might be an overlap in the reactivity of complexes containing the $Fe(CO)_xNO$ and $Co(CO)_{x+1}$ (X=2,3) metallic fragments.

Indeed, $Fe(CO)_3NO^-$ and $Co(CO)_4^-$ are both weak nucleophiles, which is to be contrasted with the high nucleophilic power of the isostructural and isoelectronic dianion $Fe(CO)_4^{2-}$ (94). Furthermore, $HFe(CO)_3NO$ and $HCo(CO)_4$ behave as strong acids and a literature survey revealed also common features in their reactions with dienes and carbonyl compounds. Both yield η^3 crotyl complexes upon reaction with butadiene (90) as depicted below.

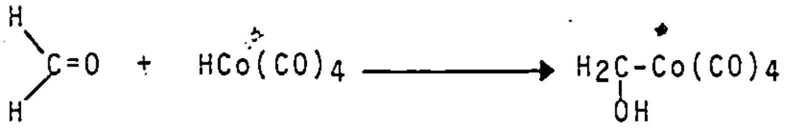
The cobalt hydride reaction with butadiene afforded



and the iron nitrosyl hydride with butadiene afforded the isoelectronic n^3 allyl 16 (in that case 2a was generated in situ by protonation of the anion 1).



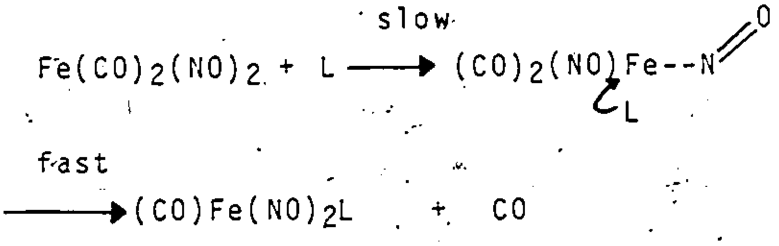
In the reaction of the iron hydride with butadiene an interesting byproduct, the n^3 allyl derivative 18; was formed. Its formation may be explained in a straightforward manner as resulting from the reaction of 2a with acetone (the acetone comes from the preparation of anion 1) (90) to give complex 17 followed by the incorporation of butadiene to give 18. That being the case, the mode of addition of hydride 2a on the ketonic function would be identical to that of $HCo(CO)_4$ on formaldehyde shown below (191).



These similarities in reactivity prompted us to initiate a more detailed investigation of the chemistry of iron nitrosyl hydrides (8-11). With respect to reactivity, such compounds should be attractive to study.

The introduction of a nitrosyl group in the metal coordination sphere could be advantageous with respect to substitution reactions (12-22, 29-31). Because of the dual nature of the nitrosyl group, the possibility of a change in the bonding mode during a reaction could facilitate the access of an external ligand to the metal coordination sphere (28). The ability of the nitrosyl group to serve either as a one electron (as in the complex $[IrCl(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ (185)) or a three electron donor (as in the complex $[IrH(NO)(P(C_6H_5)_3)_3]^+ClO_4^-$ (186)) has been well established from X-ray studies.

The conversion of linear to bent NO is believed to require only a small amount of energy (23-27, 187). The conversion can be either spontaneous (188) or induced by the addition of an external ligand (189). In particular, substitution reaction of CO ligands in coordinatively saturated nitrosyl complexes frequently proceed along an associative pathway such as the reaction depicted below (111):



$$Fe(CO)_2(NO)_2 + L \xrightarrow{\text{slow}} (CO)_2(NO)\underset{L}{Fe}\text{--}N{=}O \xrightarrow{\text{fast}} (CO)Fe(NO)_2L + CO$$

$L=P(C_6H_5)_3$ for example

In such reactions this linear $\leftrightarrows$ bent conversion is thought to arise in order to prevent the formation of a 20 electron intermediate during the addition of the phosphine ligand to the metal coordination sphere. It is significant to note also that the replacement of a CO by a NO could result in the labilisation of the remaining CO's towards further substitution reaction. For example, although $L_2Fe(CO)_3$ is inert to substitution with respect to phosphites, $L_2Fe(CO)_2NO^+$ readily reacts at room temperature with phosphites (181) having a small cone angle to yield substituted derivatives as depicted below.

$$L_2Fe(CO)_3 \xrightarrow[-\ CO]{+\ NO^+} [L_2Fe(CO)_2(NO)]^+ \xrightarrow[-\ CO]{+\ L} [L_3Fe(CO)(NO)]^+$$

$L=P(OCH_3)_3$ for example

From those results, it can be inferred that the presence of an NO ligand may enhance in some cases the accessibility of an external ligand to the metal coordination sphere. This is a key requirement for catalytic activity (32).

This work concerning the synthesis and the exploration of the reactivity of iron nitrosyl hydrides was initiated in order to obtain answers to two fundamental questions.

- What is the influence of the NO ligand on the accessibility of the coordination sphere of the metal.
- What are the minimum experimental conditions to satisfy in order to initiate a study on the catalytic activities of iron nitrosyl hydrides, especially in the reactions involving synthesis gas.

The synthesis and the study of the reactivity of the new iron nitrosyl hydrides containing triphenylphosphine ligands discussed in chapter I, serves to provide answers to these questions.

Chapter II describes the reaction of hydrides with anhydrous HBF_4 and the synthesis of a "pseudo coordinatively" unsaturated complex.

Finally, chapter III discusses the synthesis of transition metal monoanions $[Fe(CO)_x(NO)(L)_y]^-$ $(x+y=3)$ and the intermediacy of a metal formyl complex.

Iron pairing phenomena observed for these monoanions is discussed in the appendix.

CHAPTER I

Synthesis of Iron Nitrosyl Hydrides

INTRODUCTION

The transition metal hydrides containing CO ligands form a large class of compounds. However, those containing the nitrosyl ligand have not received much attention. Only a small number is presently known. Information concerning the methods of preparation and some pertinent data are presented in table I (page 15). The methods used for the synthesis of these transition metal nitrosyl hydrides have been organized into four general categories: 1) Substitution of a one electron ligand 2) Substitution of a two electron ligand 3) H elimination and 4) Protonation.

1. Substitution of a one electron ligand

A useful method for preparing transition metal hydride complexes, consists of reacting a metal complex with hydroborate or aluminate salts (44). In some cases hydrides generated by this method can best be prepared starting from the respective metal halide complex.

Some possible complications should be considered in utilizing these hydridic reagents. In a particular case, when a monohydride is desired, the initially formed hydride complex may react with hydrogen liberated in the reaction or with solvent molecules to give an unexpected polyhydrido complex. For example, alcoholic sodium borohydride has been used to obtain polyhydrido complexes of cobalt (52) and of iron (53).

$$CoCl_2.6H_2O + L\ (excess) + NaBH_4 \longrightarrow H_3CoL_3$$

$$FeCl_2.2H_2O + L\ (excess) + NaBH_4 \longrightarrow H_4FeL_3$$

L=Phosphorus ligand

In both cases it is believed that part of the reduction is occurring by hydrogen transfer from the solvent.

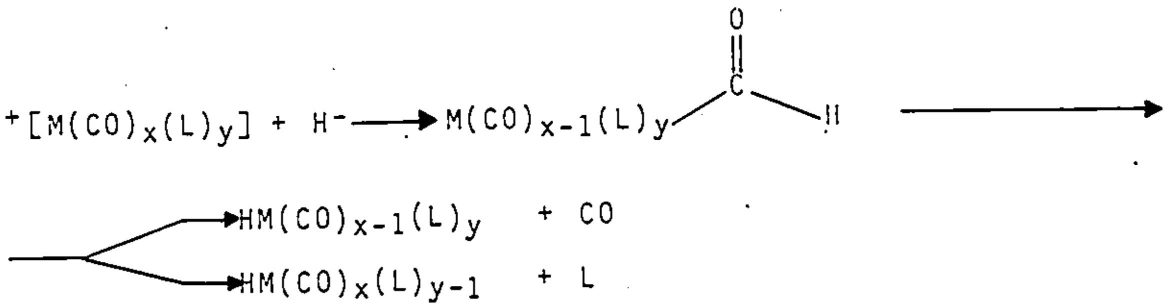
Although hydroborates and aluminate salts sometimes yield the same product with a given complex, they cannot always be used interchangeably. For example, the preparation of the nitrosyl hydride I (Table I, page 15) starting from $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ and $NaBH_4$ resulted in a yield of 13%. However, treatment of the same halide complex precursor with the gentle reducing agent sodium dihydridobis (2-methoxyethoxy) aluminate in toluene at -78°C gave a yield of 61% (41). The complex is a bright green, diamagnetic solid which can be handled in air for short periods of time without the occurrence of noticeable decomposition. Similarly, $OsH(CO)(NO)(P(C_6H_5)_3)_2$ II (56) and $MnH(NO)_2(P(C_6H_5)_3)_2$ III (57) have been obtained from the corresponding chloride.

The ratio of the reactants may also influence the outcome of the reaction. This is clearly demonstrated in the reaction of $OsCl_2(PP)_2$ (PP= bis - diphenylphosphinomethane) with $LiAlH_4$; a 100% excess of $LiAlH_4$ gave trans $HOsCl(PP)_2$ while a tenfold excess gave trans $H_2Os(PP)_2$ (55). For the preparation of hydride I, the author mentioned that the optimum stoichiometric ratio of reactants was 1:1.

2. Substitution of a two electron ligand.

Reduction of a Cationic Carbonyl with Hydride (H^-)

Hydride I and II (Table I, page 15) could also be formed from the reduction of the cationic complexes $(n^5\text{-}C_5H_5)W(NO)_2(CO)^+$ and $Os(NO)(CO)(P(C_6H_5))_3^+$ respectively with $NaBH_4$. Although details of the mechanism were not given in the formation of nitrosyl hydrides I and II by reduction of their respective cationic complexes $(n^5\text{-}C_5H_5)W(NO)_2(CO)^+$ and $Os(NO)(CO)(P(C_6H_5))_3^+$ with $NaBH_4$, it is most likely that initially a metal formyl derivative was formed (58) by attack of H^- on the carbon of the CO group (59).



$$^+[M(CO)_x(L)_y] + H^- \longrightarrow M(CO)_{x-1}(L)_y\text{-}\overset{\overset{O}{\|}}{C}\text{-}H \longrightarrow$$

$$\longrightarrow HM(CO)_{x-1}(L)_y + CO$$

$$\longrightarrow HM(CO)_x(L)_{y-1} + L$$

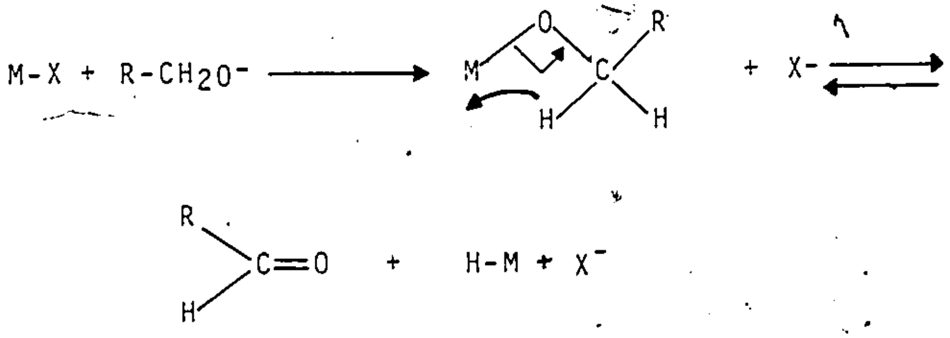
e.g. L = phosphorus ligand

Hence, in the case of hydride I (54) the initially formed formyl possibly decomposed through migration of the hydride from the formyl group with concerted loss of CO. In the case of hydride II (60), the initially formed formyl most likely decomposed through loss of $P(C_6H_5)_3$ followed by rapid hydride migration from the formyl carbon to the metal (154). A more detailed analysis of such reactions is given in the introduction of chapter III.

3. H elimination

a). Reactions with Alcohol in the Presence of Ligands in a Basic Medium

During the period 1960-65, Chatt and Shaw and also Vaska (45) established that a primary alcohol is oxidized to an aldehyde (or a secondary alcohol to a ketone) with the transfer to the metal of the α hydrogen of the initially formed coordinated alkoxide.

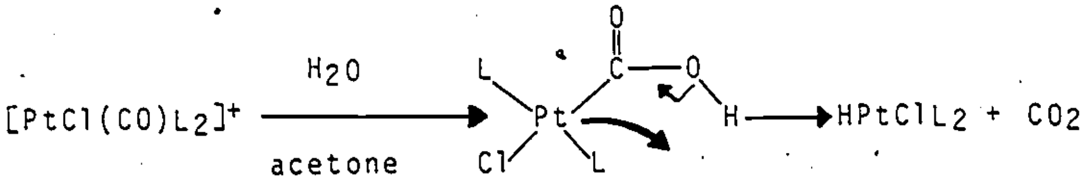


In some cases a more extensive rearrangement may occur in these types of reductions. It may involve the transfer to the metal of both hydrogen and the carbonyl group of the alkoxide to form a hydrometal carbonyl and a hydrocarbon of one less carbon than the orfginal alcohol (45).

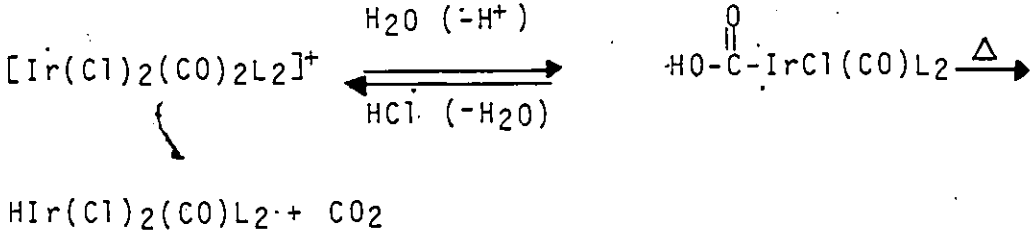
In the preparation of $HRu(NO)L_3$ IV ($L=P(C_6H_5)_3$, $P(C_6H_5)_2(CH_3)$, $P(C_6H_5)_2(CH(CH_3)_2)$, $P(C_6H_5)_2(C_6H_{11})$),the author reported their generation in high yield starting from $Ru(NO)Cl_3L_2$ with refluxing ethanolic KOH in the presence of excess L (50). Similarly the osmium hydride $HOs(NO)L_3$ V ($L=P(C_6H_5)_3$, $P(C_6H_5)_2(CH_3)$) was prepared using 2-methoxy-ethanol as the solvent.

b) Hydrolysis of Metal Cations

The generation of a hydridometal complex by the hydrolysis of cationic metal carbonyls was first demonstrated by Fischer (63) who isolated $HMn(CO)_5$ in the hydrolysis of $Mn(CO)_6^+$. Less than a decade after, the results of a kinetic study, done by Clark and Jacobs (64) on the reaction of trans-$Pt(Cl)(CO)(P(C_2H_5)_3)_2^+BF_4^-$ with water to give the hydride $HPtCl(P(C_2H_5)_3)_2$, were consistent with a mechanism involving a carboxy intermediate from which the hydride is obtained with evolution of carbon dioxide.

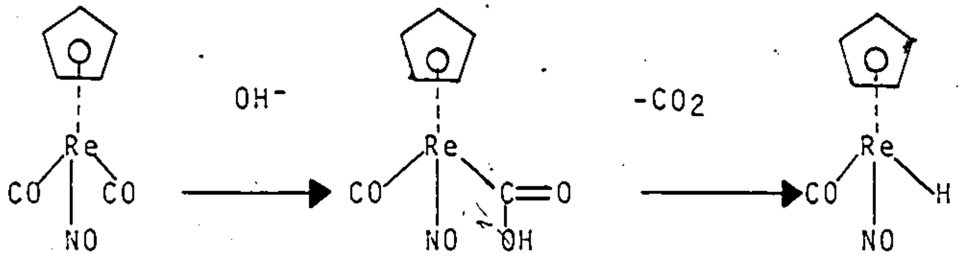


A carboxy derivative of iridium was obtained by Deeming and Shaw (65) by treatment of the corresponding cationic complex with water. Treatment of this carboxy derivative with acid restored the cationic complex and its pyrolysis gave an hydride complex.



From the reaction of $[(n^5\text{-}C_5H_5)Re(CO)_2NO]^+$ with triethylamine in water-acetone, Stewart (66) reported the preparation of the rhenium nitrosyl hydride $(n^5\text{-}C_5H_5)ReH(CO)(NO)$ VI in 60% yield. The proposed mechanism involved a nucleophilic attack of the hydroxide ion (or water) at the carbonyl carbon. The resulting carboxylate intermediate formed underwent decarboxylation to give the neutral hydride with evolution of carbon dioxide.

$$(CH_3CH_2)_3N + H_2O \rightleftharpoons (CH_3CH_2)_3NH^+ + OH^-$$



This rhenium hydride (an orange liquid) has a relatively high thermal and oxidative stability. The author indicated that practically no decomposition was observed after heating the hydride at 90°C for twenty hours in a sealed tube.

4. Protonation

A variety of uncharged complexes may be protonated with various acids (44) such as anhydrous hydrogen halides, concentrated sulfuric acid, perchloric acid, acetic acid, etc., to form a hydrido cation. In most circumstances, the anion of the acid is not coordinated but remain in the product as a counter-ion of the hydrido cation.

Reaction conditions can significantly alter the course of such reactions. For example, $Ni(dppe)_2$ (dppe = bis-diphenylphosphinoethane) and aqueous acids produced hydrogen and $Ni(dppe)_2^{2+}$ salts (67) while anhydrous acids gave the $[HNi(dppe)_2]^+$ cation (68). Furthermore, the reaction product may depend on the reaction temperature as in the case of $Os_3(CO)_{12}$ and concentrated sulfuric acid which gave $[HOs_3(CO)_{12}]^+$ at 25°C (69) and $[HOs(CO)_5]^+$ at 100°C (70).

The iridium complex $Ir(NO)(P(C_6H_5)_3)_3$ is protonated by non-complexing acids to form the stable hydrides $[IrH(NO)(P(C_6H_5)_3)_3]^+Y^-$ VII ($Y=ClO_4$, BF_4, PF_6) (71, 72). The iridium complex $Ir(NO)(P(C_6H_5)_3)_3$ is regenerated on addition of bases to the hydrides. These salts occurred in several crystalline forms differing in colour, melting point, and solid state infrared spectra. The colours of all these salts varied from green to brown with the exception of the perchlorate which also existed as almost black crystals. The neutral hydrides $IrHX(NO)(P(C_6H_5)_3)_2$ (X=CL,Br,I) are easily prepared (90% yield) by the reaction of $[IrH(NO)(P(C_6H_5)_3)_3]^+Y^-$ with lithium halides in ethanol.

A convenient synthesis of many neutral metal carbonyl hydride complexes involves the protonation of the corresponding anionic species with an acid such as sulfuric, acetic, hydrochloric etc. (44). Hydrides such as $HCo(CO)_4$ (2), $HMn(CO)_5$ (75) and $HRe(CO)_5$ (1) are readily obtained by protonation of the corresponding anions.

The iron nitrosyl hydrides $HFe(NO)(PF_3)_3$ VIII (73) and $HFe(CO)_3NO$ IX (74) were both prepared by protonation. $HFe(NO)(PF_3)_3$ was obtained in an overall yield of only 1% from $Fe(NO)_2(PF_3)_2$. $Fe(NO)_2(PF_3)_2$ was reduced to the anion $^-Fe(NO)(PF_3)_3$ and treated with H_2SO_4 to generate the hydride.

$$Fe(NO)_2(PF_3)_2 \xrightarrow{Na/Hg} {}^-Fe(NO)(PF_3)_3 \xrightarrow{H_2SO_4} HFe(NO)(PF_3)_3$$

$HFe(CO)_3NO$ was prepared from $Fe(CO)_3NO^-,Na^+$ and dry HCl. The hydride decomposed at temperatures above -45°C.

Because in exploratory studies it is more convenient to work with compounds of reasonable kinetic stability, this hydride $HFe(CO)_3NO$ was not the proper candidate to select. From a synthetic point of view, the basic problem to solve was the synthesis of iron nitrosyl hydrides of greater kinetic stability. It is known that replacement of CO's with tertiary phosphine ligands could improve the kinetic stability (80). Thus iron nitrosyl hydrides containing phosphine ligands became our target molecules. On the assumption that phosphine substitution of a CO in $HFe(CO)_3NO$ could compete effectively with its decomposition, the simple synthetic route to investigate was the protonation of the anion $Fe(CO)_3NO^-$ in the presence of a suitable phosphine.

TABLE I Survey of Nitrosyl Hydride Complexes

COMPLEX	PREPARATION		Ref.
	Substitution of one electron ligand $M\text{-}X + H^- \longrightarrow M\text{-}H + X^-$		
$(n^5\text{-}C_5H_5)W(NO)_2H$	$(n^5\text{-}C_5H_5)W(NO)_2Cl + NaAlH_2R_2$	I	54
$OsH(CO)(NO)(L)_2$	$OsCl(CO)(NO)(L)_2 + NaBH_4$	II	56
$MnH(NO)_2(L)_2$	$M_n(NO)_2(L)_2Br + NaBH_4$	III	57
$R = OCH_2CH_2OCH_3$ $L = P(C_6H_5)_3$			
	Substitution of two electrons ligands $^+M(CO)_x(L)_y + H^- \longrightarrow HM(CO)_{x-1}(L)_y + CO$ $^+M(CO)_x(L)_y + H^- \longrightarrow HM(CO)_x(L)_{y-1} + L$		
$(n^5\text{-}C_5H_5)W(NO)_2H$	$(n^5\text{-}C_5H_5)W(NO)_2(CO)^+ + NaBH_4$	I	54
$OsH(CO)(NO)(L)_2$	$Os(NO)(CO)L_3 + NaBH_4$	II	60
$L = P(C_6H_5)_3$			
	H elimination (a) $M\text{-}X + R\text{-}CH_2O^- \longrightarrow$ $M\text{-}OCH_2R \longrightarrow M\text{-}H + RCHO$		
$RuH(NO)(L)_3$	$Ru(NO)(Cl)_3(L)_2 + KOH + EtOH + L$	IV	50
$OsH(NO)(L)_3$	$Os(NO)(Cl)_3(L)_2 + KOH + CH_3OCH_2CHOH + L$	V	
$L = P(C_6H_5)_3$ etc.	(b) $M(CO)^+ + OH^- \longrightarrow M\text{-}C\text{-}OH$ $\longrightarrow H\text{-}M + CO_2$		
$(n^5\text{-}C_5H_5)Re(CO)(NO)H$	$(n^5\text{-}C_5H_5)Re(CO)_2(NO)^+ \xrightarrow[\text{acetone - }H_2O]{(CH_3CH_2)_3N}$	VI	66
	Protonation $M + H^+ \longrightarrow {}^+M\text{-}H$		
$[HIr(NO)(P(C_6H_5)_3)_3]Y$ $Y = ClO_4, BF_4$ or PF_6	$Ir(NO)(P(C_6H_5)_3)_3 + HY \longrightarrow$	VII	71-72
	$M^- + H^+ \longrightarrow HM$		
$HFe(NO)(PF_3)_3$	$^-Fe(NO)(PF)_3)_3 + H^+ \longrightarrow$	VIII	73
$HFe(CO)_3NO$	$^-Fe(CO)_3NO + H^+ \longrightarrow$	IX	74

RESULTS

In 1965, the first example of a complex containing the $[Fe(CO)(NO)(P(C_6H_5)_3)_2]$ metallic moiety was reported (77). The complex, $CF_3COFe(CO)(NO)(P(C_6H_5)_3)_2$ was obtained by the protonation of anion $Fe(CO)_3NO^-,Na^+$ 1 in ether at -65°C with a 40 fold excess of trifluoroacetic acid in the presence of two equivalents of triphenylphosphine. Under these conditions, no reaction intermediate was observed.

We found that addition of a modest 1.5 equivalents of trifluoroacetic acid to a stirred ice-cold (water-ice bath) ether solution of anion 1 and five to six equivalents of triphenylphosphine in the same solvent yielded the new iron nitrosyl hydride $HFe(CO)(NO)(P(C_6H_5)_3)_2$ 4 which precipitated from the solution as a mixture with most of the sodium trifluoroacetate within 2½ hours (Rc 1) (Rc = reaction; also note that the formulae of the compounds 1 to 12 are summarized in scheme II, page 32).

Rc 1

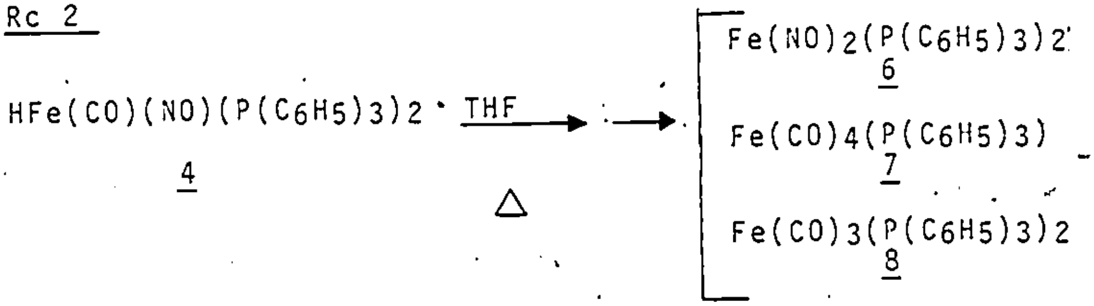
$$\underset{\underline{1}}{Fe(CO)_3NO^-,Na^+} + 1\ CF_3COOH + 2\ P(C_6H_5)_3 \xrightarrow[0°C]{Et_2O} \longrightarrow$$

$$\underset{\underline{4}}{HFe(CO)(NO)(P(C_6H_5)_3)_2} + CF_3COO^-,Na^+ + 2\ CO$$

The solid was filtered out, washed with ether and dried under vacuum. Selective extraction of the residue with benzene at room temperature followed by crystallization in benzene/pentane afforded hydride <u>4</u> in 65-70% yield as a microcrystalline orange solid solvated with benzene. When the crystalline solid was kept under high vacuum of a mass spectrometer, removal of the solvate molecule of benzene occurred. Single crystals suitable for an X-ray study were obtained from recrystallization in CS_2/hexane (10). The compound in the solid form was routinely stored under argon at room temperature, though no oxidation was observable after it was exposed for several months in contact with air. However its solutions were more air sensitive. The compound dissolved in a number of solvents such as benzene, THF, acetone, chloroform and carbon disulfide but was sparingly soluble in acetonitrile and ether.

On refluxing hydride <u>4</u> in THF, a thermal degradation occurred within four hours. The mixture of the degradation products consisted of the dinitrosyl <u>6</u> and carbonyls <u>7</u> and <u>8</u> (Rc 2)

<u>Rc 2</u>



$$\underset{\underline{4}}{HFe(CO)(NO)(P(C_6H_5)_3)_2} \xrightarrow[\Delta]{THF} \left[\begin{array}{l} \underset{\underline{6}}{Fe(NO)_2(P(C_6H_5)_3)_2} \\ \underset{\underline{7}}{Fe(CO)_4(P(C_6H_5)_3)} \\ \underset{\underline{8}}{Fe(CO)_3(P(C_6H_5)_3)_2} \end{array} \right.$$

They were readily identified by infrared spectroscopy and analytical thin layer chromatography. No attempt was made to separate the compounds on a preparative scale.

The structure of the disubstituted hydride 4 was established by NMR, IR and elemental analysis. A large high field shift in proton NMR is the best single diagnostic property for a hydrogen linked to a transition metal. In a number of cases it has made possible detection of M-H bonds formed in solution when the complex could not be isolated (79,80).

The proton NMR in C_6D_6 at 37°C with TMS as internal reference, indicated the resonance of the hydrido ligand which appeared as a 1:2:1 binomial triplet (J(P-H)= 80 Hz) centered at δ = -5.0 ppm (δ (H-Fe)). The phosphorus resonance in C_6D_6 as solvent with 85% H_3PO_4 as reference placed in a coaxial tube indicated: δ P = +77 ppm, doublet J(P-H) = 80 Hz. No significant changes in the proton NMR δ and J values were noted when other solvents such as $CDCl_3$ or CH_2Cl_2 were used. Also no change was observed when the temperature was lowered down to -50°C, indicating that the compound is stereochemically rigid.

The infrared spectra of most hydride complexes show bands in the region 1700 - 2300 cm^{-1} for the M-H stretching frequency (81). No Fe-H vibration was observed in the spectrum of hydride 4. Strong peaks at 1915 cm^{-1} and 1690 cm^{-1} (THF) in the infrared spectrum proved the presence of the carbonyl and nitrosyl groups respectively (Table II, page 30). The ν (NO) value was similar to that of other derivatives containing the $(P(C_6H_5)_3)_2Fe(CO)(NO)$ fragment, suggesting a similar mode of bonding. A X-ray single crystal analysis carried on a single crystal of 4 demonstrated unequivocally the presence of a linear Fe-N-O sub unit (10).

Although the protonation of anion 1 in ether was routinely used for the preparation of hydride 4, different approaches were also studied.

A second route to hydride 4 was investigated by modifying the introduction of tertiary phosphine and the hydrido ligand on the iron. In this case a triphenylphosphine ligand was introduced on the iron before protonation (scheme 1, page 20). Such a procedure was achieved by converting anion 1 into bis (iron tricarbonyl nitrosyl) mercury 13 (82) which underwent carbonyl substitution with triphenylphosphine to give the derivative bis (iron dicarbonyl nitrosyl triphenylphosphine) mercury 14. Reduction of complex 14 with sodium amalgam in THF, afforded anion 57 (structure discussed in chapter III). Ten equivalents of triphenylphosphine was added to the filtered yellow solution of anion 15 and 1.5 equivalent of trifluoroacetic acid was added dropwise at room temperature. The anion reacted rapidly with concomitant gas evolution to generate hydride 4 within ten minutes.

Scheme I

$$\underset{\underline{1}}{Fe(CO)_3NO^-,Na^+} + \tfrac{1}{2}\,Hg(CN)_2 \xrightarrow{-NaCN} \tfrac{1}{2}\,\underset{\underline{13}}{Hg\,[Fe(CO)_3NO]_2} \xrightarrow[+L]{-CO}$$

$$\tfrac{1}{2}\,\underset{\underline{14}}{Hg[Fe(CO)_2(NO)L]_2} \xrightarrow[Na/Hg]{THF} \underset{\underline{57}}{Fe(CO)_2(NO)L^-,Na^+} \xrightarrow[THF,L(excess)]{CF_3COOH}$$

$$\longrightarrow \quad \longrightarrow \quad \underset{\underline{4}}{HFe(CO)(NO)L_2} + CF_3COO^-,Na^+$$

$L=P(C_6H_5)_3$

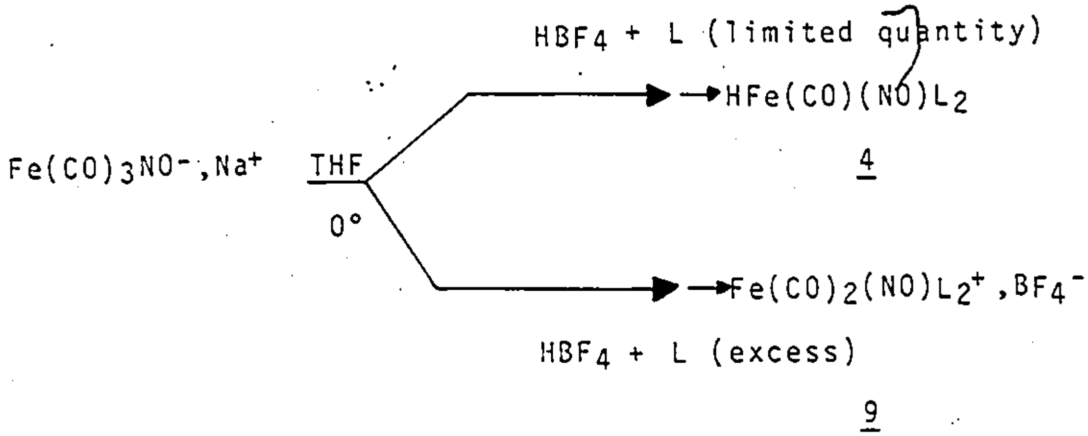
The volume of the solution containing hydride 4 was reduced under vacuum and the precipitation was completed by the addition of ether. The solid residue was filtered and hydride 4 was isolated in 32% yield, after selective extraction with benzene and crystallization in benzene/pentane (hydride contains benzene solvates). It is important to indicate that protonation with trifluoroacetic acid in THF starting from anion 1 was unsuccessful. Contrary to anion 1, anion 57 is protonated with trifluoroacetic acid in THF.

A third route to hydride 4, involving the protonation of anion 1 with anhydrous HBF_4 (HBF_4/Acetic anhydride) (83), showed that the nature of the reaction product was a function of the relative concentration of the acid and the phosphine with respect to the concentration of anion in solution.

Protonation of anion 1 in THF with a limited amount (1.5 equivalent) of anhydrous HBF_4 in the presence of 2.5 equivalents of triphenylphosphine, generated hydride 4 (Rc 3). The homogeneous solution was brought to dryness under vacuum at room temperature. The residue was washed with ether and extracted with benzene followed by crystallization in benzene/pentane which yielded 30% of hydride 4.

However, when the ratio HBF_4:$P(C_6H_5)_3$:$Fe(CO)_3NO^-,Na^+$ was modified, the reaction diverted towards the formation of the cation 9 (Rc 3). On acidification of an ice cold THF solution of anion 1 with excess anhydrous HBF_4 (5.5 equivalents) in the presence of five equivalents of triphenylphosphine, cation 9 precipitated as a mixture with $NaBF_4$ with concomitant gas evolution. The reaction was completed after stirring at room temperature for approximately eight hours. The solid was filtered out, washed with THF, dried under vacuum and extracted with chloroform. Crystallization in $CHCl_3$/pentane yielded 50% of cation 9. The infrared spectrum (Table II, page 30) of cation 9 was in agreement with IR data reported in the literature for the same compound (84).

Rc 3

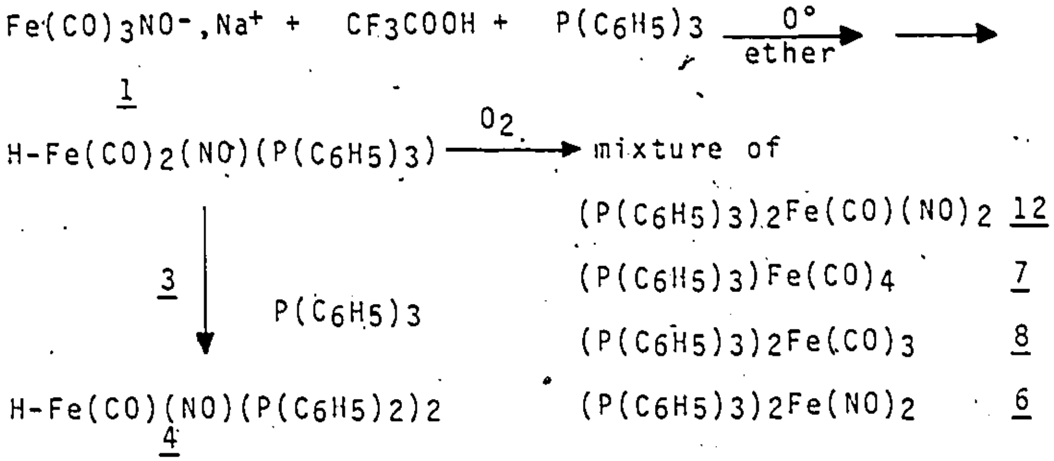


L = $P(C_6H_5)_3$
(For details of suggested mechanism, see page 32)

IR monitoring of the reaction mixture revealed the formation and slow disappearance of an intermediate with ν (CO)'s coincident with those of the dicarbonyl hydride 3 (scheme 2, page 32) (vide infra; absorption due to AcOH and Ac_2O obscured the 1700-1800 cm^{-1} region) making this compound a potential direct precursor of cation 9. It is most likely in this case that not enough free (unprotonated) phosphine was available for further rapid CO substitution and conversion to hydride 4. A detailed analysis will be given in the discussion section of this chapter.

The formation of the monocarbonyl hydride 4 starting from the tricarbonyl anion 1 required two CO substitution reactions. This substitution reaction must occur after the protonation step since the anion is unreactive toward triphenylphosphine in non acidic solution. Provided these reactions proceed at reasonably different rates, the possibility of stopping the reaction prior to the incorporation of a second phosphine ligand was investigated. Indeed, on addition of 1.2 equivalent of trifluoroacetic acid to an ice cold solution of anion 1 and approximately one equivalent of triphenylphosphine in ether, the generation of hydride 3 in situ was almost instantaneous (Rc 4). Unfortunately every attempt to isolate the hydride was frustrated by decomposition during the work up.

Rc 4



The formulation given was based upon the results of a spectroscopic study carried out directly on the protonated solutions. The ν (CO) (2020 and 1960 cm^{-1}) and ν (NO) (1755 cm^{-1}) agreed well with those of other derivatives containing the $Fe(CO)_2(NO)(P(C_6H_5)_3)$ fragment (Table II, page 30). A single crystal structure of a related compound, the mercuric derivative $Hg(Fe(NO)(CO)_2(P(C_2H_5)_3))_2$ (86), had established unequivocally the linear mode of bonding of the NO ligand. In the proton NMR, the hydrido ligand resonance appeared as a doublet at δ = -3.5 ppm (J = 12 Hz) at higher field than TMS. Extensive and reversible broadening of the signal was observed upon raising the temperature from -30°C to 0°C. Despite a small peak relative to unreacted triphenylphosphine (δ P= -5.1 ppm), the ^{31}P (^{1}H decoupled mode) spectrum consisted of a single line at δ = +64.6 ppm. The solutions were extremely air sensitive and darkened rapidly on contact with a limited amount of air. The decomposition products $(P(C_6H_5)_3)Fe(CO)(NO)_2$ 12, $(P(C_6H_5)_3Fe(CO)_4$ 7 and small quantities of $(P(C_6H_5)_3)_2Fe(NO)_2$ 6 and $(P(C_6H_5)_3)_2Fe(CO)_3$ 8 were the only products formed containing CO and/or NO. Hydride 4 was also formed and precipitated from the solution during this degradation, presumably through CO substitution by a free phosphine ligand liberated during the degradation. Where all precautions to exclude air were taken, the kinetic stability of 3 in the solutions where it had been generated was not increased greatly. At low temperatures (-75°C) hydride 3 was stable for several hours. However at room temperature, degradation to the monometallic degradation products 6, 7, 8, and 12 (+ hydride 4) resulted within one hour. In some circumstances, a rate enhancement of the decomposition was observed. For example a simple filtration through a tygon tubing could provide the rate enhancement. A likely hypothesis for such an observation is the presence of impurities which could have initiated a decomposition implicating radical intermediates, in a manner similar to that found very recently for $HCo(CO)_4$ (87).

On addition of an excess of triphenylphosphine (five equivalents) to a solution of hydride 3, hydride 4 precipitated with concurrent gas evolution (Rc 4, page 24). Through IR monitoring of the solution, hydride 3 was completely consumed after fourty minutes of reaction time. Small amounts of the compounds 4, 6, and 7 were detected by IR and TLC of the solution. The solid residue was filtered out, washed with ether and extracted with benzene. Crystallization in benzene/pentane yielded 64% of hydride 4.

Furthermore, hydride 3 could also be obtained by displacing one phosphine ligand of 4 with carbon monoxide. On passing carbon monoxide through a THF solution containing hydride 4 (room temperature) for twenty minutes, the infrared spectrum of the solution indicated a partial conversion into hydride 3 (Rc 5, page 27). Passing argon through the same solution demonstrated the partial reversibility of the carbonylation reaction. Hydride 4 was regenerated, but was accompanied with some formation of the degradation products 6, 7, 8, and 12.

Rc 5

$$\underset{\underline{4}}{\text{H-Fe(CO)(NO)(L)}_2}\ \overset{\text{CO}}{\underset{\substack{\text{argon}\\ \text{THF}}}{\rightleftarrows}}\ \underset{\underline{3}}{\text{H-Fe(CO)}_2\text{(NO)L}} + \text{L}$$

$L = P(C_6H_5)_3$

With the presence of an excess of triphenylphosphine in the reaction medium, the displacement of the phosphine ligand by carbon monoxide was completely inhibited.

In order to form a hydride substituted by a phosphine ligand different than a triphenylphosphine ligand, anion 1 was protonated in the presence of bis-diphenylphosphinoethane (dppe).

To a stirred ice cold THF solution of anion 1 and 1.2 equivalent of dppe was slowly added 1.5 equivalent of anhydrous HBF_4. After stirring one hour at 0°C and ½ hour at room temperature the homogeneous solution was subjected to vacuum until complete evaporation of the THF. The yellow residue was washed with ether and extracted with benzene. Crystallization in benzene/CH_3CN afforded H-Fe(CO)(NO)(dppe) in 60% yield (dppe = bis-diphenylphosphinoethane).

The proton NMR and IR are in agreement with the proposed structure. The IR spectrum showed two strong peaks at 1940 cm^{-1} (ν CO) and 1710 cm^{-1} (ν NO). The proton NMR ($CDCl_3$) indicated: δ (C_6H_5) 7.82 - 6.82 ppm (multiplet), δ (CH_2) 2.04 ppm (doublet, J(P-H)=18 Hz), δ (Fe-H) = -3.35 (triplet, J(P-H)=26 Hz), TMS as reference (This dppe substituted hydride was prepared by Dr. J.Y. Mérour in our lab).

When it was exposed to air, oxidation was apparent within a month. As it was the case for hydride 4, solutions were more air sensitive. It could be dissolved in THF, CH_2Cl_2, $CHCl_3$, benzene and was sparingly soluble in CH_3CN and in ether. Similar to the trialkyl and triaryl phosphite cobalt hydride which showed a high barrier to ligand dissociation (89), the dppe substituted hydride did not undergo ligand dissociation after passing CO through its THF solution for more than twelve hours.

TABLE II

IR DATA

Complex		νCO cm^{-1}	νNO cm^{-1}	solvent
$HFe(CO)(NO)L_2$	4	1915s	1690s	THF
		1910s	1680s	$CHCl_3$, CH_2Cl_2
		1910s	1690s	KBr
$HFe(CO)_2(NO)L$	3	2020m, 1960s	1755s	Ether
$L_2Fe(CO)_2NO^+, BF_4^-$	9	2050s 1990s	1790s	CH_2Cl_2, $CHCl_3$
$LFe(CO)_4$	7	2060, 1975, 1945		THF, CH_2Cl_2
$L_2Fe(CO)_3$	8	1890		THF, CH_2Cl_2
$L_2Fe(NO)_2$	6		1720s, 1670vs	THF, CH_2Cl_2
Selected Complexes	Ref			
$CF_3COFe(CO)(NO)L_2$	(77)	1931vs	1710vs	KBr
$CNFe(CO)(NO)L_2$	(138)	1930	1700	nujol
$Hg(Fe(CO)_2(NO)L)_2$	(175)	1989, 1963	1725	KBr
		1924, 1917	1715	
$IHgFe(CO)_2(NO)L$	(175)	2000, 1943	1746	$CHCl_3$

vs = very strong, s = strong, m = medium

$L = P(C_6H_5)_3$

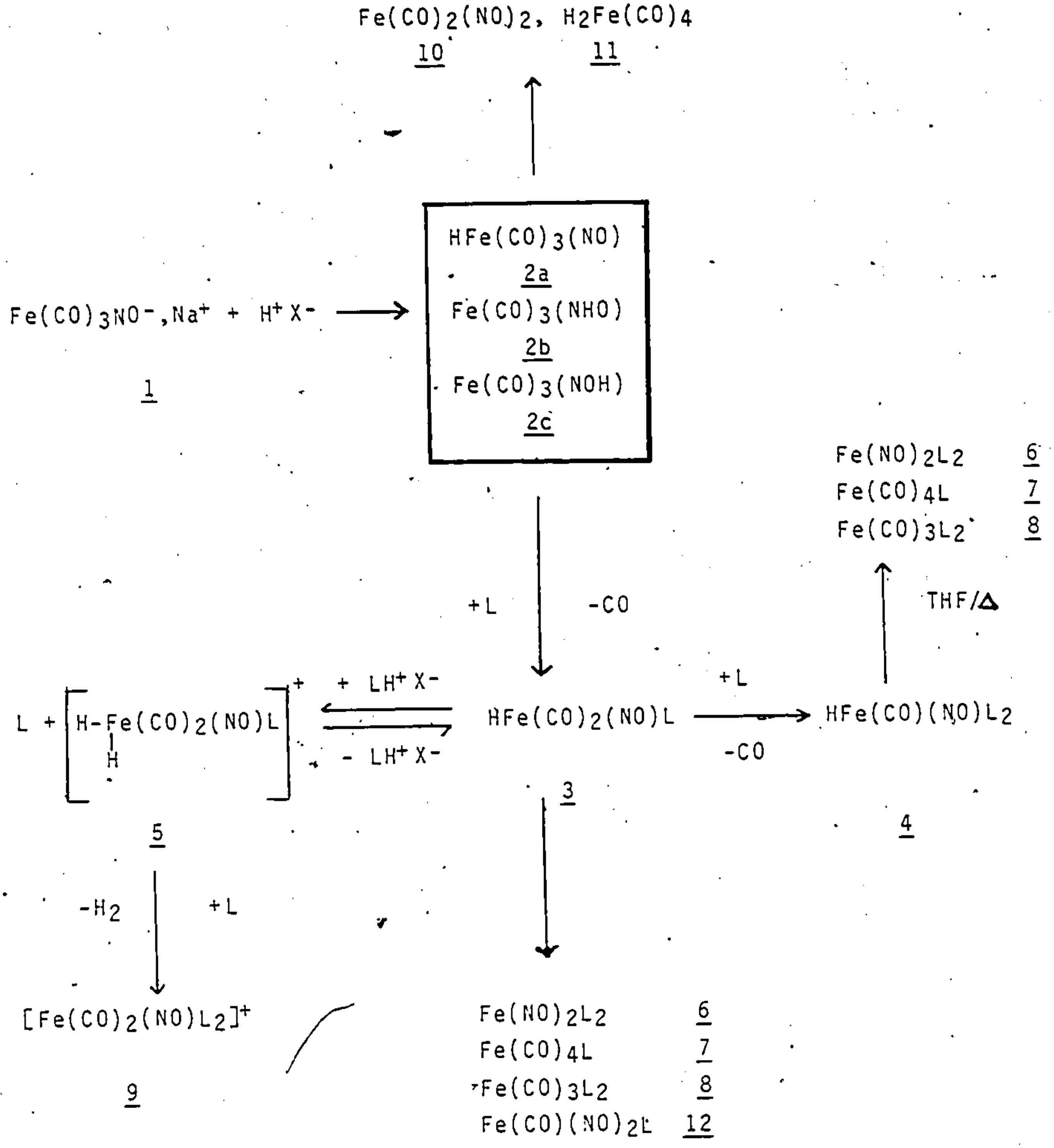
DISCUSSION

Analysis of Conceivable Reaction Pathways Implicated in the Protonation Reactions

1-A Protonation Leading to Hydride $HFe(CO)(NO)(P(C_6H_5)_3)_2$ 4

In 1962, Heiber and Beutner reported the protonation of the sodium salt of anion 1 at low temperature (-60°C) in dimethyl ether with anhydrous HCl (74). After work up at low temperature, a very unstable liquid formulated as 2a was isolated. Sometimes a violent decomposition occurred at -45°C, giving a mixture of the dinitrosyl 10 and the carbonyl dihydride 11.

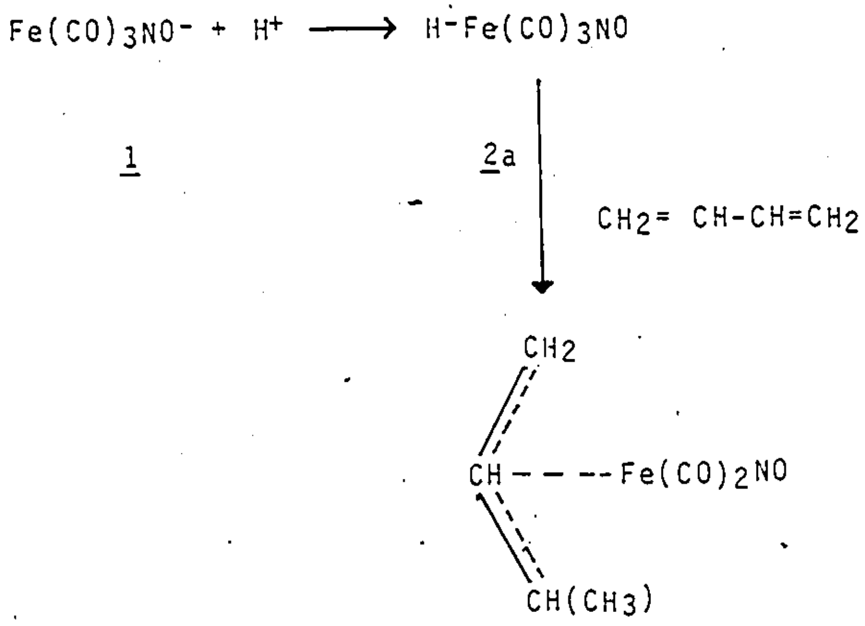
Scheme II



$L = P(C_6H_5)_3$
Δ = thermolysis

In 1967, the chemical evidence for the in situ generation of hydride 2a was provided by Pauson (90). As mentioned earlier in this chapter, Pauson reported that when hydride 2a was generated in ether from the protonation of anion 1 with acetic acid at -75°C in the presence of butadiene (followed by slow warming to room temperature), the n^3 crotyl complex 16 (Rc 6) was formed.

Rc 6



16

Rc 7

Similarly, we observed that when the anion 1 was protonated (ether, 5°C) with trifluoroacetic acid in the absence of triphenylphosphine, formation in a few seconds of the volatile $Fe(CO)_2(NO)_2$ was observed ($H_2Fe(CO)_4$ was not detected under these conditions). This qualitative observation can be taken as a good evidence for the efficient generation of the hydride $HFe(CO)_3NO$ under these "reactional" conditions.

However, the analysis of the solvent dependency of both the qualitative rate of protonation and the solution structure of anion 1 makes it uncertain that it was hydride 2a which actually underwent the first substitution reaction. In sharp contrast with the protonation in ether, when THF was used as solvent, the disappearance of anion 1 became a **much slower process.** IR monitoring of the THF solution showed no significant decrease in the intensities of the ν (CO) and ν (NO) shortly after acidification (~ 15 minutes). There was however a slow decomposition reaction taking place after several hours.

Change in the acid strength of the acid species (CF_3COOH or $[(C_6H_5)_3PH^+, CF_3COO^-]$ if it is the actual protonating species) can be expected in principle. But such an effect is difficult to evaluate, since this change of solvent also **induces a modification of the solution structure of anion 1.** This modification of the nature and the state of aggregation of the ion pairs formed between $Fe(CO)_3NO^-$ and the counter cation Na^+ was studied by Pannell (93). The solution structure of anion 1 and its monosubstituted derivative $P(C_6H_5)_3Fe(CO)_2NO^+$ will be discussed in more detail in the appendix (page 98).

It is enough to say at this point, that there is an equilibrium between tight (A) and loose (B) ion pairs and that in the tight ion pairs the cation is interacting specifically with the oxygen of the nitrosyl ligand (Rc 8).

Rc 8

$$\underset{\underline{A}}{Fe(CO)_3\,NO^- \sim\!\sim Na^+} + S \rightleftharpoons \underset{\underline{B}}{Fe(CO)_3NO^-(S)Na^+}$$

In THF, both tight ion pair species A and solvated ion pair species B are present in observable amounts. In ether, only the tight ion pair species is observed. However, the tight ion pair species found in THF is different from that in ether. The interaction in the tight ion pairs is greater for the species present in ether than those in THF. Alteration in the chemical reactivity induced by ion pairing phenomena has been demonstrated in many circumstances. It has been demonstrated very elegantly in the alkylation reactions of $Fe(CO)_4{}^{2-}$, $2Na^+$ (94) or in the Lewis acid catalysed alkyl migration in $R\text{-}Fe(CO)_4{}^-, Na^+$ (95).

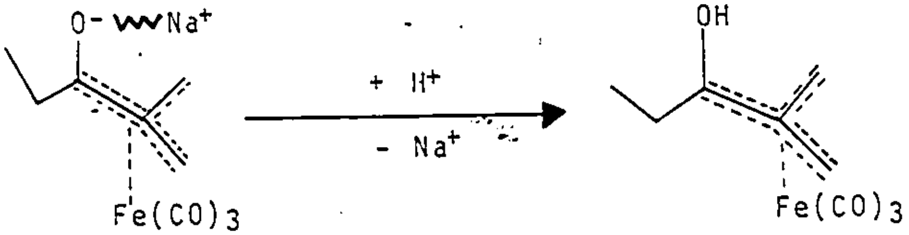
In NMP, $Na_2Fe(CO)_4$ reacted predominantly as a highly nucleophilic solvent separated complex. In THF the less reactive tight ion pairs (by a factor of 2 X 10^4) were the dominant solution species. The X-ray studies (96) showed that in the tight ion pairs the cation was interacting predominantly with the oxygen of the carbonyl ligand. Whenever the interaction $\text{M-CO}\sim\sim\text{Na}^+$ was weakened (tight ⟶ solvated ion pairs) the π back bonding from the metal to the CO decreased and the electronic density on the metal increased. In the alkylation reaction, the reaction center was the metal. Thus, the solvent dependency on the rate of reaction parallels the solvent influence on the electronic density of the reactive center, which is the metal in this case.

More closely related to the present situation is the recently reported (97) dependency upon ion pairing of the rate of disappearance of anion <u>1</u> in its reaction with methyl iodide. In all cases, formation of a metal-carbon bond was postulated. The rate was increasing in the order $k\ (\text{ether}) < k\ (\text{THF})$ and again paralleling the increase of the electronic density on the metal or conversely a decrease of the electronic density on the NO ligand.

Such an influence of ion pairing phenomena could be equally important in the protonation reaction of anion 1. The basicity of each of the sites in the anion which are available for protonation (metal or ligand) is dependent upon the electronic distribution which in turn is affected by the nature and the extent of the cation-anion interaction. As the binding of Na^+ to NO increases, the electronic distribution in the anion is modified which in turn alters the basicity of all the sites which are available for reaction with H^+. If that is the case, protonation at the metal in ether is the less likely site since it is the less basic center. Consequently, kinetic protonation at the N and/or O atoms of the nitrosyl ligand (which is the most basic site in ether) leading to the intermediate 2b and/or 2c cannot be disregarded.

Indeed, an example of a protonation reaction (98) in which protonation was precisely directed at the site of the metalate (the oxygen center of the organic ligand) which interacted specifically with the cation Na^+, in tight ion pairs is shown in Rc 9.

Rc 9



Furthermore, the electrophilic attack of an acid at the nitrogen of an NO ligand to convert the coordinated nitric oxide to a coordinated nitrosyl hydride HNO was observed in complexes such as $OsCl(CO)(NO)(P(C_6H_5)_3)_2$ (99) and $ReH(NO)_2(P(C_6H_5)_3)_2$ (100). Recently also was reported the protonation at the oxygen of a bridging CO ligand in iron (101, 102) and in cobalt clusters (103) (Rc 10).

Rc 10

(a) $HFe_3(CO)_{11}^- + H^+ \longrightarrow HFe_3(CO)_{10}(COH)$

(b) $Co_3(CO)_{10}^-, + H^+ \longrightarrow Co_3(CO)_9(COH) \longrightarrow HCo(CO)_4 + \frac{1}{2}\, Co_4(CO)_{12}$

It is interesting to note that in the contact ion pairs formed by $HFe_3(CO)_{11}^-$, the site of preferential interation was also a bridging CO. In the cobalt case H migration to the metal was observed during cluster fragmentation (103). (It is a possiblity that hydride 2a could be generated in this way from 2b and/or 2c).

In summary, because of the uncertainty in the number of species actually present after protonation of anion 1, the complex implicated in the very fast substitution leading to hydride 3 cannot be identified with certainty as being $HFe(CO)_3NO$ 2a.

It is important to note however that the fast substitution rate of the reaction is very reminiscent of the one converting $HCo(CO)_4$ 19 into $HCo(CO)_3(P(C_6H_5)_3)$ 20 (104). At the time this reaction was discovered a dissociative mechanism was suggested as depicted in Rc 11.

Rc 11

$$\underset{\underline{19}}{H\text{-}Co(CO)_4} \rightleftarrows HCo(CO)_3\square + CO \xrightarrow{L} \underset{\underline{20}}{HCo(CO)_3L}$$

$L = P(C_6H_5)_3$

The low ranking of the hydride ligand in the cis-labilizing series (105) has led to doubt about the dissociative nature of this reaction. A radical chain mechanism, demonstrated to occur in complexes such as $HRe(CO)_5$ (106) and $HM(CO)_3Cp$ (M=Mo,W) (107), has been suggested instead (87). With $H\text{-}Mn(CO)_5$ however, in addition to a radical chain process, a paralleling reaction converting the hydride into an unsaturated formyl was also suggested (109), although it is generally assumed that the reverse reaction is thermodynamically more favored (see Chapter III). It is worthy to note also that ~~a~~ similar conversion into an unsaturated formyl was postulated in the $HCo(CO)_4$ catalysed synthesis of oxygenates from synthesis gas ~~at~~ 200°C (110).

Furthermore, with the ability of the nitrosyl ligand to serve either as a one electron or a three electron donor (23-27, 111), associative and/or dissociative (105, 112) reaction pathways are also possible with these iron nitrosyl hydrides.

Hence, it is clear that more detailed studies are needed before attempting to understand the nature of the substitution reactions involved in the formation of these iron nitrosyl hydrides.

Some differences in chemical behaviour between the two families of hydrides $HFe(CO)_x(NO)L_y$ and $HCo(CO)_uL_v$ ($x + y = 3$, $u + v = 4$; L = phosphorus ligand) are worthy of note. Contrary to $P(OC_6H_5)_3$ (113) or $P(OCH_2)_3C\text{-}CH_3$ (114) which underwent facile carbonyl polysubstitution with $HCo(CO)_4$, triphenylphosphine underwent only monosubstitution (114). The formation of a monosubstituted complex on reacting $P(C_6H_5)_3$ is to be contrasted with the ease of formation of the disubstituted iron nitroysl hydride 4. **This behavior in the case of iron implies the availability of lower activation energy in the reaction pathways leading to polysubstitution.**

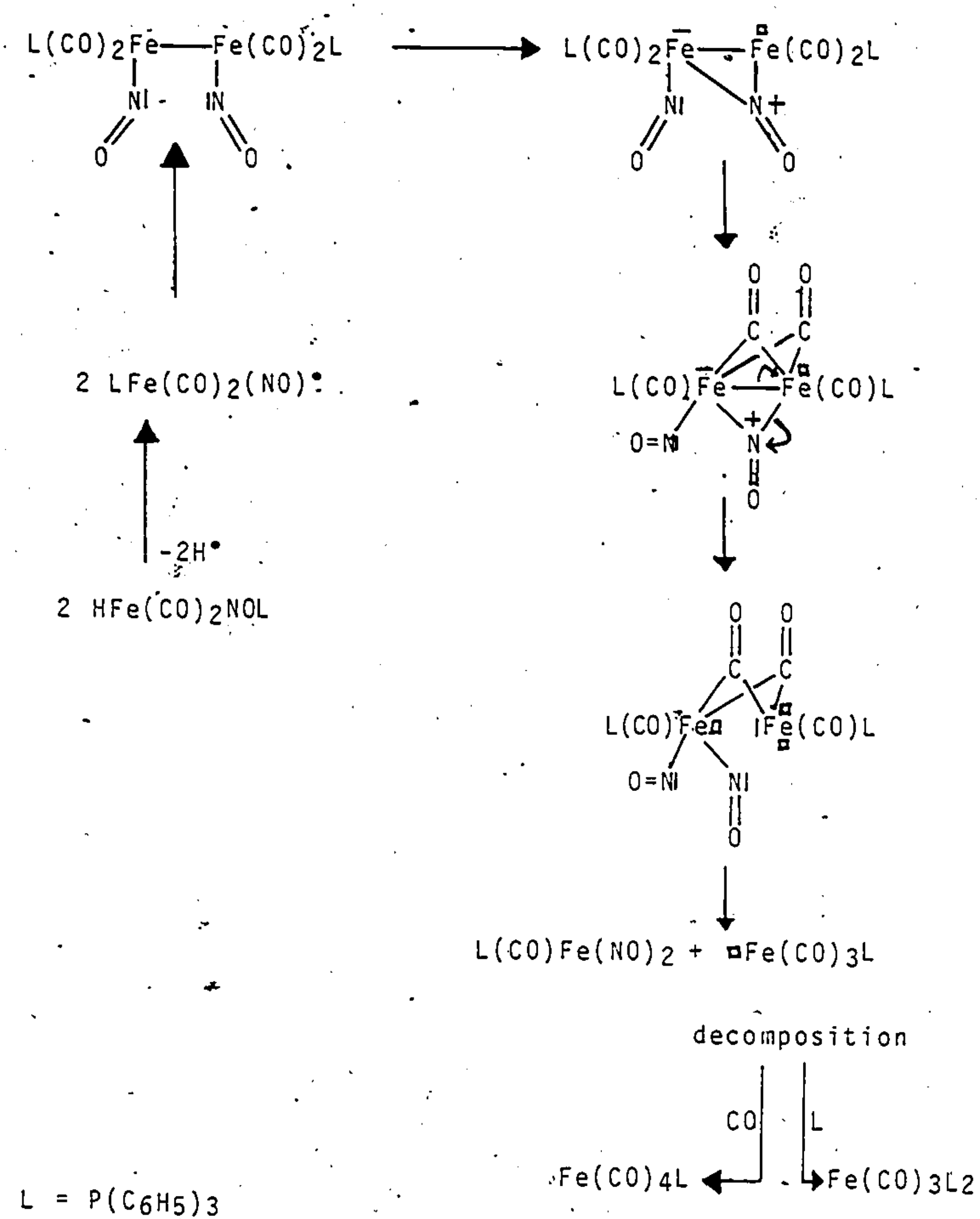
A second and most striking difference is found in the nature of the thermal decomposition products. Decomposition of monohydride complexes are generally known to afford molecular hydrogen and metal-metal bonded metallic dimers. Indeed metallic dimers were obtained in the thermal decomposition of $HCo(CO)_3(L)$ (L = CO (108); L = $P(C_6H_5)_3$ (104); L = $P(OC_6H_5)_3$ (115)).

$$2\ HCo(CO)_3L \longrightarrow L(CO)_3Co{-}{-}Co(CO)_3L + H_2$$

L = CO, $P(C_6H_5)_3$, $P(OC_6H_5)_3$

This is to be contrasted with the thermal decomposition of iron nitrosyl hydrides <u>2a</u>, <u>3</u> and <u>4</u> $HFe(CO)_x(NO)(P(C_6H_5)_3)_y$ (x + y = 3; y = 0, 1, 2) where in no case could the formation of an iron-iron dinitrosyl dimer be detected. Instead monometallic degradation products resulting from ligand redistributions were characterized. Among these degradation products were found dinitrosyl derivatives, demonstrating the occurence of a nitrosyl exchange reaction at some point in the reaction pathways. For such an exchange reaction to occur, the formation of a dimer appears to be a prerequisite (116, 117). Hence it suggests that this decomposition reaction actually yields iron metallic dimers. **<u>But contrary to cobalt dimers, iron dimers are apparently unstable with respect to irreversible and fast NO (and CO) exchanges, inducing a fragmentation into new mono metallic complexes.</u>**

The following decomposition pathway for the iron dimers is suggested.



L = $P(C_6H_5)_3$

In this mechanism the bent mode for the nitrosyl ligand was used, but the linear mode could also apply in most intermediate steps.

Other observations are consistent with this view. A similar redistribution of ligands has been observed when preparing bimetallic complexes such as $(NO)((PC_6H_5)_3)_2=Ni-Fe(CO)_3(NO)$ or $(NO)_2(P(C_6H_5)_3)Co-Fe(CO)_3(NO)$ and it was suggested that the migration of ligands between the metals follow an intermolecular mechanism with $P(C_6H_5)_3$ and an intramolecular one with CO and NO (117). Also the scrambling of the two ligands in $(n^5-C_5H_5)W(NO)_2H$, when treated with equimolar amounts of $HCo(CO)_4$ or $(n^5-C_5H_5)W(CO)_3H$, was believed to proceed via a bimetallic intermediate (41). More closely related is the one electron oxidation of metalates yielding metallic radicals which dimerize subsequently (118), in the absence of steric effects (119). Also in the one electron electrochemical oxidation of $Co(CO)_4^-$,

$$2Co(CO)_4^- \xrightarrow{(1+1)\bar{e}} 2Co(CO)_4^\bullet \longrightarrow Co(CO)_4\text{—}Co(CO)_4$$

the dimer $Co_2(CO)_8$ was obtained but with $Fe(CO)_3NO^-$,

$$2Fe(CO)_3NO^- \xrightarrow{(1+1)\bar{e}} 2Fe(CO)_3NO^\bullet \longrightarrow \underset{\underline{10}}{Fe(NO)_2(CO)_2} + \text{unidentified decomposition products}$$

formation of dinitrosyl 10 resulted (120, 121). Furthermore occurence of electron transfer has been recognized in some reactions between alkyl halides and metalates (122); metallic dimers are often formed as byproducts in quantities depending on the nature of both reagents. In that context, formation of variable amounts of dinitrosyl products was reported already for various alkylation reactions of anion 1 (90). In a case, related to our study, it was observed that the monosubstituted anion $(P(C_6H_5)_3)Fe(CO)_2(NO)^-,Na^+$ reacted with allyl bromide (8) to form alkylation products but only a mixture of 6,7,8, and 12 was produced in the reaction with $Br-CH_2-CH=C=CH_2$ (123). Finally we have demonstrated that reactions between some cationic and anionic iron nitrosyl complexes afforded only monometallic degradation products (chapter III), contrary to the related reactions in the cobalt family yielding dimers.

In the context of catalytic reactions implicating H_2 or synthesis gas, the potential usefulness of mononitrosyl iron complexes should be critically dependent upon:

1) the possibilities to prevent the formation of dimers or

2) the ability of the metallic dimers to react fast enough with suitable reagents prior to irreversible degradation due to nitrosyl (carbonyl) transfer.

The study of the reduction of iron nitrosyl cations detailed in chapter III showed that it was indeed possible to have situations in which the reactivity of the metallic dimer towards suitable reagents was fast enough to compete effectively with degradation.

Protonation Leading to Cation
$[Fe(CO)_2NO(P(C_6H_5)_3)_2]^+$ 9

A conceivalbe route to cation 9 was depicted in scheme II, page 32. As mentioned, protonation of anion 1 may lead to 2a, 2b and/or 2c where one or more of these species may undergo substitution to form ultimately hydride 3. The ease of its detection through IR monitoring of the reaction mixture on protonation of anion 1 with anhydrous HBF_4 in the presence of $P(C_6H_5)_3$ in the molar ration 1/5.0/5.5 indicated that free triphenylphosphine was not present in sufficient amount to convert hydride 3 into 4. Thus, most of the free phosphine must have been converted into the protonated form. Formation of cation 9 under these conditions may occur subsequent to proton delivery by a protonated phosphine which would generate ultimately the dihydride intermediate 5. The free triphenylphoshine liberated is now available to occupy the vacant coordination site liberated by molecular hydrogen in the reductive elimination step.

Such a protonation step by a protonated phosphine has been considered previously (85).

CHAPTER II

Reaction of Hydrides with Anhydrous HBF_4
and
Synthesis of a "Pseudo Coordinatively" Unsaturated Complex $[(NO)Fe(CO)(P(C_6H_5)_3)_2]^+$

INTRODUCTION

In the previous chapter, the anion $Fe(CO)_3NO^-$ 1 (scheme II, page 32) was shown to be a convenient starting material in the synthesis of iron nitrosyl hydrides substituted by triphenylphosphine ligands.

Protonation of anion 1, in the presence of triphenylphosphine, yielded hydride 3 which was converted into the hydride 4 or into the cation 9, depending upon the reaction conditions. In the previous discussion, the possibility that the dihydride 5 might be a reaction intermediate had been suggested.

In their own right, dihydride complexes are known to form a very interesting class of compounds. Their involvement in some catalytic hydrogenation reactions of unsaturated molecules has been firmly established (32, 33). Depending on the corresponding catalytic precursor, neutral dihydrides such as

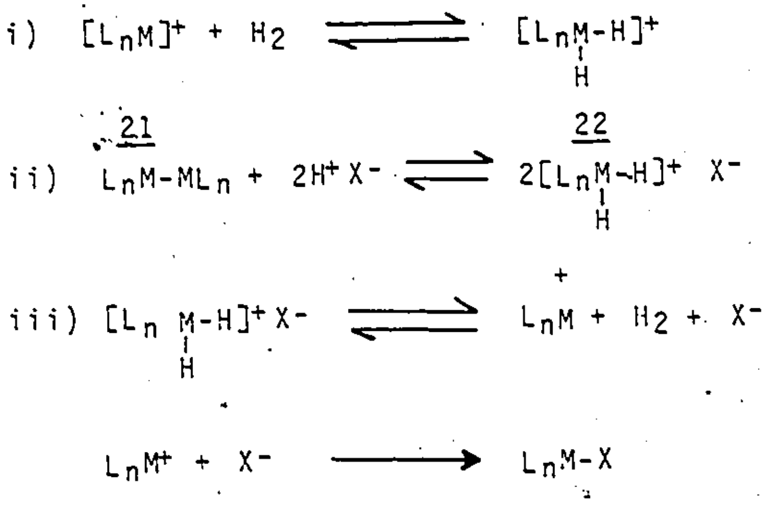
$H_2Rh(Cl)(P(C_6H_5)_3)_3$ (33) as well as cationic dihydrides such as $[H_2Rh(P(C_6H_5)_3)_3]^+$ (33) and $[H_2Ir(olefin)_2(P(C_6H_5)_3)_2]^+$ (124) were the active intermediate.

Recently, these dihydride complexes were recognized as key intermediates in the industrially important "water-gas-shift-reaction" (WGSR) ($H_2O + CO \quad H_2 + CO_2$) (33, 125). Again in these catalytic reactions, depending upon the nature of the catalytic system, neutral (i.e. $H_2Fe(CO)_4$ (126)) or cationic (33, 125) dihydride complexes were implicated.

In order to complete the information in the literature regarding synthesis and reactivity of iron nitrosyl dihydride complexes, we were prompted to investigate in more detail different approaches to the generation of such important complexes.

If indeed our analysis of the reaction pathway leading to the cation 9 was correct, instability of such dihydrides with respect to the reductive elimination of H_2 can be expected. The equilibrium depicted by Rc 12 was convenient for studying the factors affecting the thermodynamic stability of the dihydride complex 22 with respect to the unsaturated metallic fragment 21 and molecular hydrogen.

Rc 12



i) $[L_nM]^+ + H_2 \rightleftharpoons [L_n\underset{H}{M}\text{-}H]^+$

21 22

ii) $L_nM\text{-}ML_n + 2H^+X^- \rightleftharpoons 2[L_n\underset{H}{M}\text{-}H]^+ X^-$

iii) $[L_n\underset{H}{M}\text{-}H]^+X^- \rightleftharpoons \overset{+}{L_nM} + H_2 + X^-$

$L_nM^+ + X^- \longrightarrow L_nM\text{-}X$

L = ligand

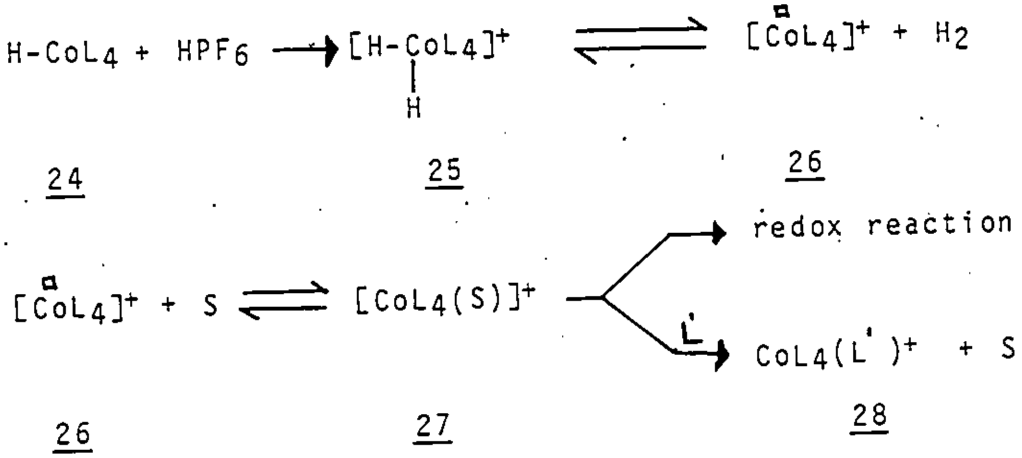
All the available results have shown a shift of the equilibrium toward the dihydride species 22, as the electron releasing ability of the auxillary ligand (L) (consequently the basicity of the metallic fragment) was increased (88). Hence, an increase in thermodynamic stability of dihydride similar to 5 was expected as the number of phosphorus ligands was increased at the expense of the carbonyl ligands.

For this reason, the two hydrides $HFe(CO)(NO)(dppe)$ 23 and $HFe(CO)(NO)(P(C_6H_5)_3)_2$ 4, both containing one additional phosphorus ligand than hydride 3, were selected as the neutral precursors. In the situation.

where insufficient stability would be achieved in the cationic dihydride complexes generated by protonation, very reactive fragments were expected to be formed following the spontaneous reductive elimination of molecular hydrogen.

The generation of a cationic dihydride by protonation of a neutral monohydride, which was expected to be formed in our case, could lead to complications depending on the nature of the reaction medium. This is clearly illustrated in Rc 13. Protonation of the hydrido cobalt complex 24 (127) with HPF6 yielded the dihydride 25.

Rc 13



$$\underset{24}{\text{H-CoL}_4} + \text{HPF}_6 \longrightarrow \underset{25}{[\text{H-}\underset{\substack{|\\\text{H}}}{\text{Co}}\text{L}_4]^+} \rightleftharpoons \underset{26}{[\overset{\square}{\text{Co}}\text{L}_4]^+} + \text{H}_2$$

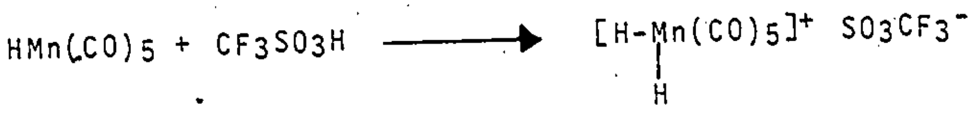
$$\begin{tikzcd}[column sep=small] \underset{26}{[\overset{\square}{\text{Co}}\text{L}_4]^+ + \text{S}} \arrow[r, shift left] & \underset{27}{[\text{CoL}_4(\text{S})]^+} \arrow[l, shift left] \arrow[r] \arrow[dr, "\text{L}'"'] & \text{redox reaction} \\ & & \underset{28}{\text{CoL}_4(\text{L}')^+} + \text{S} \end{tikzcd}$$

Slow decomposition of the dihydride 25 was observed in donor solvents such as acetonitrile or in the presence of an additional two electron ligand L , such as a tertiary phosphite. Kinetic data suggested a dissociative pathway leading to the coordinatively unsaturated cation 26. The proof that the equilibrium 25 $\rightleftharpoons$ 26 laid far to the left (on complex 25 side) was demonstrated by the solid-state reaction of the coordinatively unsaturated cation 26 (prepared by another route) with molecular hydrogen (128). However, in solution, the stabilization of this reactive cation by a solvent molecule (for example CH_3CN) shifted the equilibrium to the right, allowing other reactions such as the formation of the penta coordinated species 27 to take place at a reasonable rate.

The ability of a metallic fragment to bind molecular hydrogen, as shown in Rc 12i, could only be tested under conditions where other reaction pathways such as reductive elimination and ligand addition were not readily available. The use of an acid in which the conjugated base would act only as a weak ligand was required. It was assumed that the HBF_4 /acetic anhydride mixture used previously had such properties.

Very recently, as our work was already submitted for publication (9), a similar approach was followed in the protonation of the manganese hydride 29 (Rc 14) by CF_3SO_3H in that solvent (129).

Rc 14



$$HMn(CO)_5 + CF_3SO_3H \longrightarrow [H\text{-}\underset{\displaystyle H}{\underset{|}{Mn}}(CO)_5]^+ \; SO_3CF_3^-$$

29 30

$$\longrightarrow H_2 + [Mn(CO)_5]^+, CF_3SO_3^-$$

31

The spontaneous H_2 reductive elimination from the dihydride 30, which was a likely reaction intermediate, afforded the "unsolvated" specie 31 in which the interaction with the ligand $CF_3SO_3^-$ was minimal. The reactivity of these species in solution toward addition of another ligand, such as carbon monoxide, **demonstrated the ready accessibility of an additional coordination site in the metal**. According to the author, their study provided the first example of a "pseudo coordinatively unsaturated complex".

RESULTS

Unfortunately, several attempts to protonate the hydride H-Fe(CO)(NO)(dppe) 23 (in the presence of CO gas or excess dppe) in THF with anhydrous HBF_4 were continuously met with failure. Although the hydride was completely consumed, only $Fe(NO)_2(dppe)$ was characterized.

Despite the failure to protonate with the hydride 23, encouraging results were obtained on protonating the hydride $HFe(CO)(NO)(P(C_6H_5)_3)_2$ 4 (scheme III, page 70). On dropwise addition of 1.2 equivalents of anhydrous HBF_4 on a stirred THF or THF:ether (1:1) solution of the hydride 4 at 0°C, precipitation of a brown powder with concurrent H_2 loss (verified by mass spectroscopy) (9) resulted. The precipitate was collected, washed with ether and dried in vacuo (yield = 86%). The same result was obtained by adding anhydrous HBF_4 to a stirred suspension of hydride 4 in ether.

The reaction medium must be perfectly anhydrous. Traces of water in the reaction medium caused immediate decomposition of the solid suspended in THF. The decomposition proceeded with gas evolution accompanied with solubilization of the solid material. Carbon monoxide was the only gaseous product detected by mass spectroscopy. In solution, the iron dinitrosyl complex $Fe(NO)_2(P(C_6H_5)_3)_2$ 10 was the only iron containing product characterized by infrared spectroscopy of the reaction solution.

The structure of compound 32, obtained from the protonation of hydride 4, could not be deduced directly from spectroscopic data. It was inferred from its chemical behavior in the solid state as well as in solution. All the available results favored the presence of a very easily accessible coordination site in compound 32.

Consider the reactions of compound 32 in the solid state and in solution.

1: Solid State Reactions

Under one atmosphere (approximately) of carbon monoxide, compound 32 underwent a clean solid-gas reaction. The colour gradually changed (12-24 hours depending on amount) from orange-brown to yellow during its transformation into the coordinatively saturated cation 9 $[Fe(CO)_2(NO)(P(C_6H_5)_3)_2]^+BF_4^-$, with the absence of any other compounds containing CO and/or NO ligands. Such behaviour indicated the cationic nature of compound 32.

On pressing a KBr pellet of compound 32 and recording the infrared spectrum of the metal-CO and metal metal-NO region, peaks of equal intensity at 1920 cm^{-1} and 1695 cm^{-1} were detected. This infrared pattern was identical to the neutral five-coordinate halide $BrFe(CO)(NO)(P(C_6H_5)_3)_2$ $(\underline{34})_2$ synthesized independently in this work. It is very likely that a very fast reaction between the compound 32 and the bromine anion has occurred, as the pellet was pressed. A similar solid state reaction, on pressing a KBr pellet, was recently reported with the cation $(\eta^7\text{-}C_7H_7)Mo(CO)_3^+$, BF_4^- (130).

The KBr spectra of the solid after conversion of compound 32 to the cation 9 or into the neutral halide $(\underline{34})_2$ provided no evidence which indicated the presence of a molecule of either acetic acid or acetic anhydride acting as a ligand in compound 32. The prospect that the compound 32 could be a solvent stabilized species was then ruled out. It thus seems likely that compound 32 was another example of a "pseudo coordinatively unsaturated" species with the counter anion interacting very weakly with the metal.

2A - Reactions in Solution

On dissolving compound 32 in methylene chloride or acetone, decomposition into the dinitrosyl 10 and cation 9 resulted. The formation of the cation 9 may be attributed to the reaction of the undecomposed compound 32 with liberated carbon monoxide during the decomposition. Under argon, compound 32 in the solid form underwent a slow decomposition (several days) into the same decomposition products.

Despite its instability in the above solvents, compound 32 was soluble in acetonitrile without any decomposition at room temperature. The infrared spectrum of the solution exhibited two strong peaks of equal intensity and width at 1960 cm^{-1} and 1750 cm^{-1}, corresponding to a carbonyl and a linear nitrosyl respectively. On comparing this spectrum to those of neutral iron nitrosyl complexes such as the hydride 4 or the halide $(\underline{34})_2$ (having as ligands two triphenylphosphine, one nitrosyl and one carbonyl), a shift of about 40 to 60 cm^{-1} in the ν CO and ν NO was observed. Such a shift was consistent with the presence of a positive charge in the complex (88, 134).

Indeed on addition of ether to an acetonitrile solution of compound 32, red-brown air stable crystals (for several weeks) of the cation 33 $[Fe(CO)(NO)(P(C_6H_5)_3)_2(CH_3CN)]^+ BF_4^-$, having an acetonitrile ligand in the coordination sphere, precipitated from the solution. The crystals were collected, washed with ether and dried in vacuo (80% yield).

The structure assigned to the cation 33 was consistent with NMR, IR and elemental analysis data. The proton NMR (VARIAN HA 100; $CDCl_3$ with TMS internal reference indicated; δ (ppm): C_6H_5 (7.58), CH_3CN solvate (2.05, large singlet), CH_3CN ligand (1.58 triplet (J(P-H)=2 Hz)), characteristic of a coordinated CH_3CN ligand (131)) showed the presence of a CH_3CN ligand.

These crystals were now soluble in chlorinated solvents and in acetone without any decomposition. However, decomposition into a mixture of dinitrosyl 10 and cation 9 still occured on heating these solutions of cation 33 around 40-50°C for two to four hours.

2B - Lability of Acetonitrile and Metathesis Reactions

The most prominent ligand feature of acetonitrile in transition metal complexes is the ease with which it can be replaced by other ligands (132). The rate of exchange of coordinated acetonitrile (with for example non-coordinated acetonitrile) is greatly influenced by the other ligands in the complex. A trend frequently observed in these acetonitrile complexes was the ability of the phosphorus ligands to reduce the rate of exchange. For example $[C_3F_7Fe(CO)_2(CH_3CN)_3]^+$ exchanged rapidly one acetonitrile ligand at room temperature contrary to the $[C_3F_7Fe(CO)_2(P(C_6H_5)_3)(CH_3CN)_2]^+$ which was inert to exchange (133).

Despite the presence of two phosphorus ligands in cation 33, the high lability of the coordinated acetonitrile ligand was demonstrated by its instantaneous exchange with CD_3CN in the NMR tube, a rapid disappearance of the peak at 1.58 ppm accompanied by an increase in intensity of the peak at 2.05 ppm (assigned to the uncoordinated acetonitrile) clearly indicated the lability of the coordinated acetonitrile.

This lability of acetonitrile towards substitution reactions in the solid state was demonstrated on pressing a KBr pellet of cation 33. The infrared spectrum initially exhibited the ν CO and ν NO characteristic of the cationic species which were gradually replaced (approximately half hour) by those of the neutral bromide $(\underline{34})_2$ $Br-Fe(CO)(NO)(P(C_6H_5)_3)_2$ (depending on how the pellets were pressed, solid states splitting was observed).

On many occasions these acetonitrile complexes, with the coordinated acetonitrile having a high lability, were used as precursors to a variety of species (135). The isolation in high yield of cation 32 and its ready conversion into the highly labile acetonitrile complex (cation 33), suggested that cation 33 should be a useful precursor to a variety of neutral five coordinate complexes $(NO)Fe(CO)(P(C_6H_5)_3)_2X$ (X = halide). Indeed, portionwise addition of the cation 33 to the appropriate salts (A^+, X^-) in acetonitrile afforded the respective complexes $(NO)Fe(CO)(P(C_6H_5)_3)_2X$ $(\underline{34})_n$ (n = 1, X = Cl ; n = 2, X = Br; n = 3, X = I) (Scheme III) as crystalline material in yields varying from 60 - 80% (136, 137). On addition of the salts (A^+,X^-) at room temperatures, the corresponding product instantaneously precipitated from the reaction solution as a microcrystalline colored solid. They are dark-brown relatively air stable solids, soluble in methylene chloride and acetone and sparingly soluble in acetonitrile. A decomposition to uncharactized products proceeded slowly when they were dissolved in chlorinated solvents or in acetone.

The elemental analysis for $C_{37}H_{30}FeINO_2P_2$ was consistent with the assigned structure $(\underline{34})_3$. Infrared spectra of these complexes $(\underline{34})_n$ (n=1,2,3) were also in agreement with data reported by Lalor (136) who prepared these halide complexes by a different route. However yields were not given and the iodide complex could not be obtained in pure state.

By reaction with $AgPF_6$ in acetone (with CH_3CN in the reaction medium) the halide complexes $(NO)Fe(CO)(NO)(P(C_6H_5)_3)_2X$ (X = Cl, Br or I) were converted to cation 33 (with counteranion PF_6^-), with the simultaneous precipitation of the corresponding silver halides (AgX; X = Cl, Br and I). In the absence of acetonitrile in the reaction medium the expected decomposition to dinitrosyl 10 occurred, due to the instability of coordinatively unsaturated cation 32 in acetone..

The azide complex $(NO)Fe(CO)(P(C_6H_5)_3)_2N_3$ (34)4 was also prepared, using $[(P(C_6H_5)_3)_2N]^+,N_3^-$, under similar conditions. The azide complex was characterized by infrared (136, 138) was obtained in 43% yield as a brown crystalline material.

Additional evidence of an easily accessible coordination site in cation 32 was given by the formation of cation 9 in 55% yield on protonation of hydride 4 in THF under one atmosphere of carbon monoxide and excess triphenylphosphine by anhydrous HBF_4 (139) (Rc 15).

Rc 15

$$\underset{\underline{4}}{\mathrm{H\text{-}Fe(CO)(NO)(P(C_6H_5)_3)_2}} \xrightarrow[\substack{\mathrm{P(C_6H_5)_3} \\ \text{(excess)} \\ \mathrm{CO/THF}}]{\mathrm{HBF_4}} \underset{\underline{9}}{\mathrm{BF_4Fe(CO)_2(NO)(P(C_6H_5)_3)_2}}$$

On protonation under the same conditions, except under argon atmosphere rather than CO, the expected coordinatively saturated complex $^+Fe(CO)(NO)(P(C_6H_5)_3)_3$, BF_4^- was not obtained, probably due to steric reasons (136). Instead cation <u>32</u> was formed.

Discussion

A conceivable route to cation 32 and subsequently to cation 33, starting from hydride 4, is depicted in Rc 16.

Rc 16

$$\underset{\underline{4}}{\text{H-Fe(CO)(NO)(L)}_2} + \text{HBF}_4 \xrightarrow[\substack{\text{THF} \\ \text{or THF : ether} \\ \text{or ether}}]{} \text{BF}_4^- \; {}^+\underset{\underline{35}}{[\text{H-}\underset{\text{H}}{\text{Fe}}\text{(CO)(NO)(L)}_2]}$$

$$\longrightarrow \underset{\underline{32}}{[\text{Fe(CO)(NO)(L)}_2]^+} \text{BF}_4^- + \text{H}_2 \xrightarrow{\text{CH}_3\text{CN}}$$

$$\underset{\underline{33}}{[(\text{L})_2\text{Fe(CO)(NO)(CH}_3\text{CN)}]^+ \text{BF}_4^-}$$

$\text{L} = \text{P(C}_6\text{H}_5)_3$

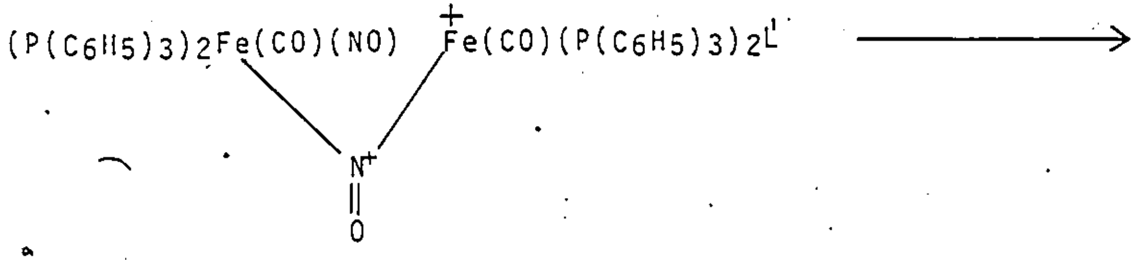
In the formation of 32 from hydride 4 the dihydride 35 could not be detected by infrared spectroscopy, but is a logical intermediate. Unlike the osmium dihydride analog $[H_2Os(CO)(NO)(P(C_6H_5)_3)]^+PF_6^-$(139), dihydride 35 was very unstable and decomposed rapidly at 0°C to the cation 32 through reductive elimination of molecular hydrogen, on treatment of hydride 4 with 1.2 equivalent of anhydrous HBF_4.

These results are in agreement with the generalization (140) that dihydrido complexes of the third-row transition elements are much more basic than their first row counterparts. The greater stabilization of the osmium dihydrido complex may be ascribed to the higher electron density in the osmium complex relative to the iron complex (88). Furthermore unlike cation 32, acetone did not cause decomposition of $[Os(CO)(NO)(P(C_6H_5)_3]^+PF_6^-$, but instead formed the acetone complex $[Os(CO)(NO)(acetone)(P(C_6H_5)_3)]^+PF_6^-$, stable in CH_2Cl_2 (139).

Formation of the dinitrosyl 10, on decomposition of cation 32 implied the intermolecular transfer of the coordinated nitrosyl group. It was shown (116, 141) that such nitrosyl transfer reactions occured through a bimetallic complex μ - nitrosyl [M(μ-NO)M1] which can be formed only if the acceptor complex possesses an easily accessible coordination site or was coordinatively unsaturated. Preceeding experimental results have shown that this was the case with cation <u>32</u>. With the information available, the decomposition mechanism of cation <u>32</u> depicted in Rc 17 is suggested.

<u>Rc 17</u>

$$\underset{\underline{32a}}{[(P(C_6H_5)_3)_2Fe(CO)(NO)(L)]^+} + \underset{\underline{32b}}{[(P(C_6H_5)_3)_2Fe(CO)(NO)(L')]^+} \xrightarrow{-L}$$



$$(P(C_6H_5)_3)_2Fe(CO)(NO)\,\overset{+}{Fe}(CO)(P(C_6H_5)_3)_2L' \longrightarrow$$

<u>36</u>

$$(P(C_6H_5)_3)_2Fe(NO)_2 + 2CO + Fe^{2+} + L + 2P(C_6H_5)_3$$

L = L' = H_2O, BF_4^-, acetone, CH_2Cl_2 or CH_3CN as examples.

The decomposition reaction involves the formation of a bimetallic intermediate bridging nitrosyl 36, which is formed by dimerization of 32a and 32b through the displacement of the ligand L. Similar decomposition products were obtained from the decomposition of the unstable iron complex $Fe(CO)(NO)(P(C_6H_5)_3)$ prepared by polarographic reduction of $Fe(CO)(NO)_2(P(C_6H_5)_3)$ (142).

Rc 18

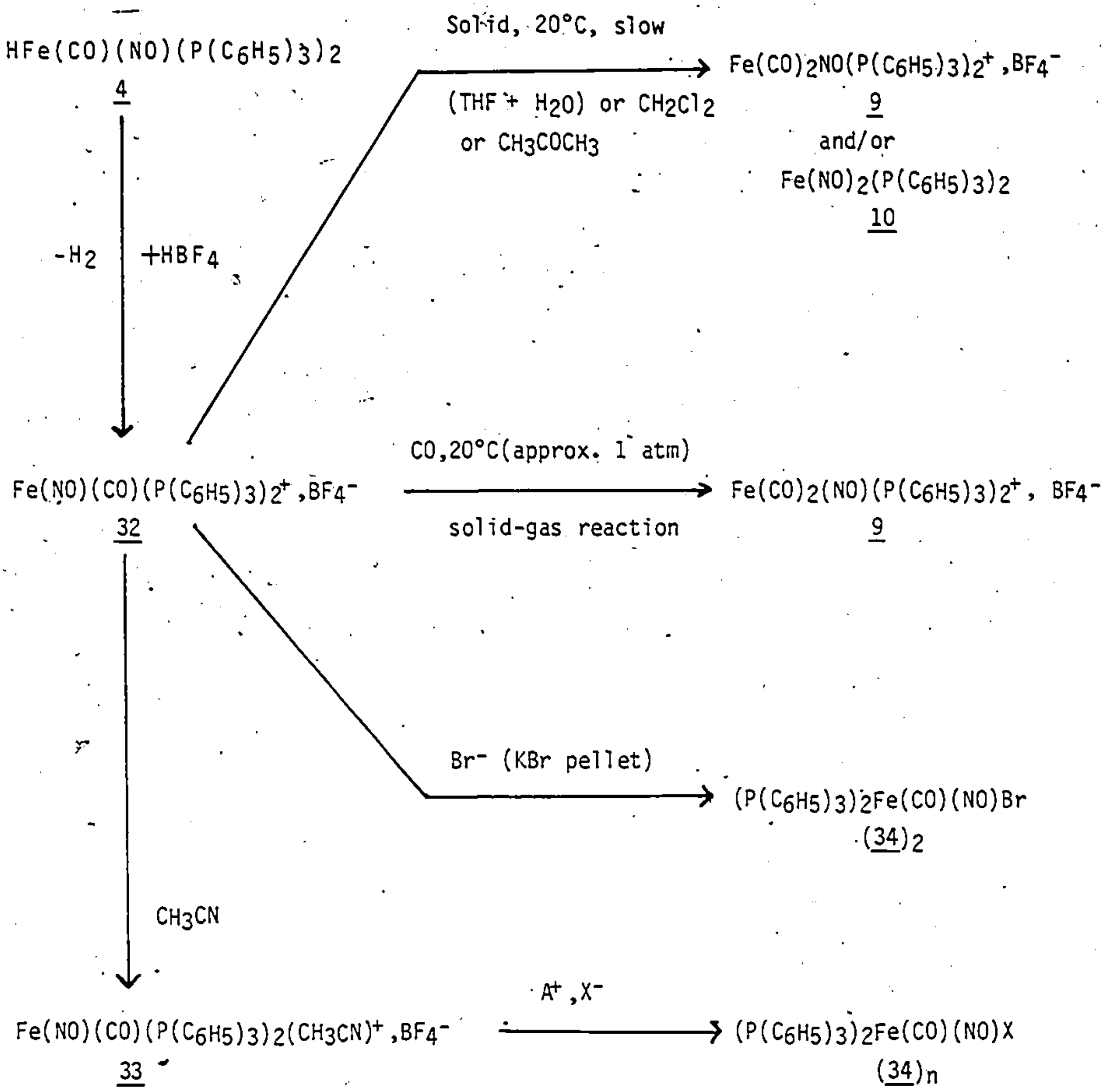
$$\begin{tikzcd}
\text{decomposition} & {[Fe(CO)(NO)_2(P(C_6H_5)_3)]^{2-}} \arrow[l, "\text{slow}"'] \\
Fe(CO)(NO)_2(P(C_6H_5)_3) + \bar{e} \arrow[r, shift left, harpoon] & {[Fe(CO)(NO)_2(P(C_6H_5)_3)]^{-}} \arrow[l, shift left, harpoon] \arrow[u] \arrow[d, "H^+"'] \\
\tfrac{1}{2}Fe(NO)_2(P(C_6H_5)_3)_2 + \tfrac{1}{2}\,Fe^{2+} + CO & Fe(CO)(NO)(P(C_6H_5)_3)]^{+} + NOH^{-} \arrow[l, "\bar{e}"']
\end{tikzcd}$$

Since carbonyl ligands also have the ability of forming bridges, the possibility of a transfer mechanism involving a bimetallic intermediate similar to 36 but containing a μ-CO bridge cannot be neglected.

Overall the decomposition caused by water can be explained by the formation of a soluble aquo (carbonyl, nitrosyl) complex ($L=L'=H_2O$) which is unstable toward dimerization by displacement, leading to the decomposition products. Formation of analogous aquo complexes of manganese were recently described in the literature (135, 143). For example, the aqua ligand in $[Mn(CO)_4(H_2O)(P(C_6H_5)_3)]^+$ were readily displaced to give the species $[Mn(CO)_4(L)(PC_6H_5)_3]^+$ (where L = CO, or $P(C_6H_5)_3$). However contrary to H_2O, acetonitrile ($L = L' = CH_3CN$) can interact sufficiently with the metal to increase the kinetic stability of the complex 32 at room temperature. Solvents such as methylene chloride, acetone and chloroform were inadequate in increasing the stability of the complex.

Worthy of note is the preparation of iron nitrosyl divalent complexes. Ruthenium complexes, of the type $RuXY_2(NO)(P(C_6H_5)_3)_2$, were prepared from their corresponding halide complexes and isolated by Laing and coworkers (137). Analogous divalent iron nitrosyls $(NO)FeXY_2(NO)(P(C_6H_5)_3)_2$ (X = Br, Y = I; X = Cl, Y = I and Br; table III for IR) were prepared in this lab by oxidation of the corresponding zerovalent complex $(NO)FeX(CO)(P(C_6H_5)_3)_2$ in methylene chloride with halogens. Unfortunately, these complexes are unstable and decomposed rapidly during work up, so they could not be obtained in pure state. However, these divalent iron nitrosyl complexes have infrared spectra similar to those of their ruthenium counterparts.

Scheme III



$n = 1$, $X^- = Cl^-$ and $A^+ = PPN^+$
$n = 2$, $X^- = Br^-$ and $A^+ = C_6H_5CH_2\overset{+}{N}(C_2H_5)_3$
$n = 3$, $X^- = I^-$ and $A^+ = Na^+$
$n = 4$, $X^- = N_3^-$ and $A^+ = PPN^+$

$(PPN^+ = P(C_6H_5)_3{=}\overset{+}{N}{=}P(C_6H_5)_3)$

Table III

Complex		ν (CO)(cm^{-1})	ν (NO)(cm^{-1})	ν (N$_3$)(cm^{-1})	Solvent
$Fe(CO)(NO)(L)_2(CH_3CN)^+,BF_4^-$ 33		1960	1750		CH_3CN
$Fe(CO)(NO)(L)_2X$	(34)n				
X = Cl	n = 1	1925	1700		CH_2Cl_2
		1920	1690		KBr
X = Br	n = 2	1930	1710		CH_2Cl_2
		1920	1695		KBr
X = I	n = 3	1930	1710		$CHCl_3$
		1925	1700		KBr
X = N_3	n = 4	1925	1670	2060	CH_2Cl_2
		1915	1680	2045	KBr
$FeXY_2(NO)(L)_2$					
X = Br, Y = I			1800		CH_2Cl_2
X = Cl, Y = I			1800		CH_2Cl_2
X = Cl, Y = Br			1830		CH_2Cl_2

L = $P(C_6H_5)_3$ and absorption strong in all cases

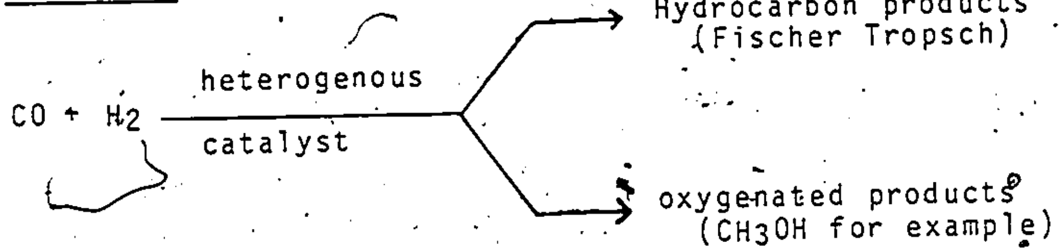
CHAPTER III

Synthesis of Transition-Metal Monoanions $[Fe(CO)_x(NO)L_y]^-$ $(x+y = 3)$; intermediacy of a metal formyl complex

INTRODUCTION

The increasing demand for energy, coupled with uncertainty and expense of imported crude oil have caused increased interest in the research for alternative sources of liquid fuels and petrochemical feedstocks. One such alternative, now being extensively investigated, is the conversion of synthesis gas (H_2 + CO mixture) obtained from coal gasification into hydrocarbons (Fischer-Tropsch (34)) or into oxygenated products (methanolization for example (61)) (Scheme IV).

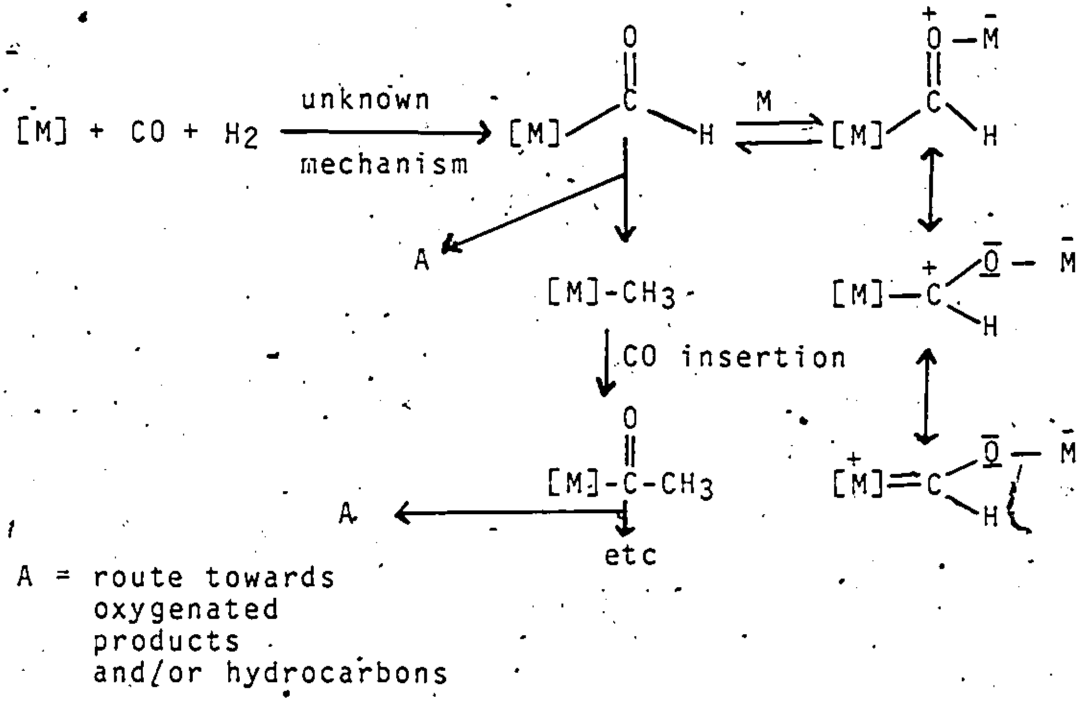
Scheme IV



One theory holds (34) that with most heterogeneous catalysts, the primary products of the reaction are straight chain alkanes, while secondary products include branched-chain alkanes, alkenes, alcohols, aldehydes and carboxylic acids. The distribution of the various products depends on both the type of catalyst and the reaction conditions employed (144).

Metal formyl complex intermediates are believed to be formed in some of these reactions (34), as depicted in the over simplified mechanism in scheme V.

Scheme V

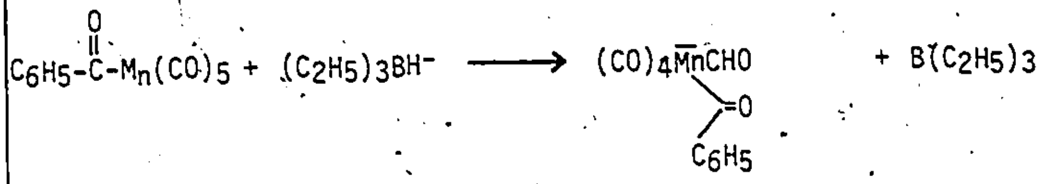
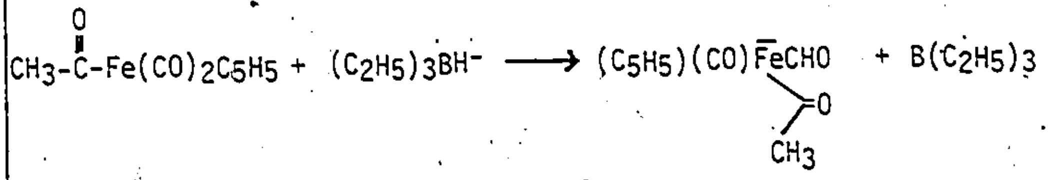


Current theories favor the idea of the interaction of the oxo oxygen of the formyl ligand with another metallic center (M') acting as a Lewis acid (bimetallic catalyst (146, 153, 190)). Such an interaction is thought to provide further stabilization of the formyl complex with respect to a mono or polymetallic carbonyl hydrido species. An additional beneficial consequence of the interaction is the enhancement of the electrophilic character of the formyl carbon atom which is an important factor in subsequent reduction of the formyl ligand.

The first formyl complex $(CO)_4FeCHO^-$ was synthesized by Collman (124) from $Fe(CO)_4{}^{2-}$ and acetic formic anhydride and was isolated as the $[N(P(C_6H_5)_3)_2]^+$ salt. Unfortunately, this route did not prove to be general.

However, in the last few years the synthesis of a variety of anionic metal formyl complexes has been achieved by treatment of neutral carbonyl compounds with limited amounts of hydride donors, such as boron hydrides. Some examples are given in Table IV.

Table IV

$L_xM(CO) + HBR_3^- \longrightarrow L_x\overset{-}{M}-\overset{O}{\overset{\|}{C}}-H + BR_3$	Ref.
 $C_6H_5-\overset{O}{\overset{\|\|}{C}}-M_n(CO)_5 + (C_2H_5)_3BH^- \longrightarrow (CO)_4\overline{Mn}C(=O)C_6H_5\,CHO + B(C_2H_5)_3$	a(147)
 $CH_3-\overset{O}{\overset{\|\|}{C}}-Fe(CO)_2C_5H_5 + (C_2H_5)_3BH^- \longrightarrow (C_5H_5)(CO)\overline{Fe}C(=O)CH_3\,CHO + B(C_2H_5)_3$	b(147)
$Fe(CO)_5 + (CH_3O)_3BH^- \longrightarrow (CO)_4\overline{Fe}CHO + B(CH_3O)_3$	c(148)
$Cr(CO)_6 + (i\text{-}PrO)_3BH^- \longrightarrow (CO)_5\overline{Cr}CHO + B(i\text{-}Pro)_3$	d(148)
$P(OC_6H_5)_3Fe(CO)_4 + (i\text{-}Pro)_3BH^- \longrightarrow P(OC_6H_5)_3(CO)_3\overline{Fe}CHO + B(i\text{-}Pro)_3$	e(151)

(a) & (b) yield measured relative to 1,2,4,5 - tetrachlorobenzene internal standard

(a) 98.4%

(b) 96.8%

(c) & (d) NMR analysis yield measured relative to toluene internal standard.

(c) 80-90%

(d) 76%

(e) By reacting six fold excess of $K^+HB(O\text{-}iPr)_3^-$ with $(CO)_4FeP(OC_6H_5)_3$ in THF followed by cation exchange of the resulting potassium salt with $[Et_4N]^+Br^-$ and 1N NaOH gave $[EtN]^+(C_6H_5O)_3P(CO)_3FeCHO^-$ as a light tan powder in 64% yield.

Recently, this potentially general methodology has been extended to the preparation of neutral metal formyl complexes from cationic metal carbonyl precursors. Some examples are given in Table V.

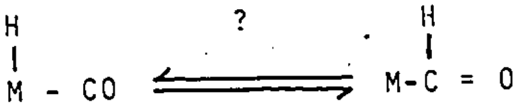
TABLE V

$[LxM(CO)]^+ + HBR_3^- \longrightarrow LxM\overset{O}{\overset{\|}{C}}-H + BR_3$	Ref.
$[(C_5H_5)Re(CO)_2NO]^+BF_4^- + (C_2H_5)BH^- \longrightarrow (C_5H_5)(CO)(NO)ReCHO + (C_2H_5)_3B$	a(37)
$[(C_6H_5)_3P)_2Ir(CO)_3]^+PF_6^- + (C_2H_5)_3BH^- \longrightarrow (C_6H_5)_3)_2(CO)_2IrCHO + (C_2H_5)_3B$	b(38)
$[(Mn(CO)_4(P(C_6H_5)_3)_2]^+PF_6^- + (C_2H_5)_3BH^- \longrightarrow ((C_6H_5)_3)_2(CO)_3MnCHO + (C_2H_5)_3B$	c(38)
$[(C_5H_5)Re(CO)(NO)(P(C_6H_5)_3)]^+BF_4^- + (C_2H_5)_3BH^- \longrightarrow (C_5H_5)(NO)ReCHO + (C_2H_5)_3B$	"d"(38)
$[(C_5H_5)Mo(CO)_3(P(C_6H_5)_3)]^+PF_6^- + (C_2H_5)_3BH^- \longrightarrow (C_5H_5)(CO)_2(P(C_6H_5)_3)MoCHO + (C_2H_5)_3B$	e(38)
$[(C_5H_5)M_n(CO)_2(NO)]^+PF_6^- + (C_2H_5)_3BH^- \longrightarrow (C_5H_5)(CO)(NO)MnCHO + (C_2H_5)_3B$	f(38)

Yield by ^1H NMR relative to an internal standard:

(a) 60% (b) 80% (c) 71% ("d") isolated yield 59% (e) 41% (f) 100%

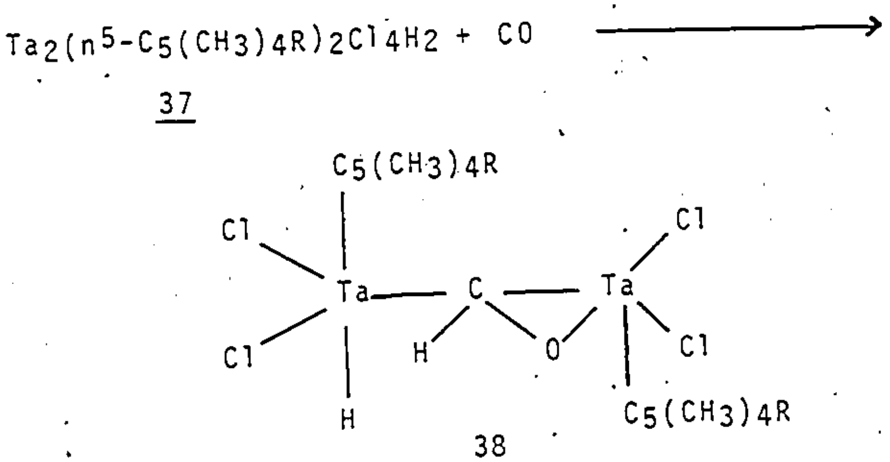
All the above systems are indirect routes to metal formyl species. At present, although suggested as a key intermediate step in the CO exchange of $HMn(CO)_5$ (109), there are no proven examples of the direct insertion of carbon monoxide into a metal-hydride bond (152).



$$\overset{H}{\underset{}{M}} - CO \xrightleftharpoons{?} M-\overset{H}{C}=O$$

However, it is important to note that very recently a dimeric tantalum hydrido formyl complex 38 (Rc 19) was isolated by Schrock (153) from the reaction of a dimeric tantalum hydride complex 37 with carbon monoxide.

Rc 19



$Ta_2(\eta^5\text{-}C_5(CH_3)_4R)_2Cl_4H_2 + CO \longrightarrow$

37

38

R = CH_3, CH_3CH_2

Contrary to the direct insertion of CO in a metal-hydride bond, the reverse reaction has received considerable experimental support. For example, the metal formyl compound 39 (Rc 20), which was generated by the addition of metal trialkoxyborohydride ($(HB(O\text{-}i\text{-}Pr)_3^-, K^+)$) to the corresponding neutral metal carbonyl, decomposed in THF at 65°C into hydride 40 (by loss of phosphite and hydride migration) and into hydride 41 (by loss of CO and hydride migration) (154).

Rc 20

$$(CH_3CH_2)_4N^+,((C_6H_5O)_3P)(CO)_3FeCHO^- \longrightarrow$$

39

$$(CH_3CH_2)_4N^+,(CO)_4FeH^- + (C_6H_5O)_3P$$

40

and $$(CH_3CH_2)_4N^+,((C_6H_5O)_3P)(CO)_3FeH^- + CO$$

41

This isomerization into the more thermodynamically stable hydride may occur at a much lower temperature, depending on the stability of the formyl. Such a situation was observed for a neutral iridium complex which cleanly decomposed at -40°C (20 minutes) into the corresponding hydride (Rc 21) (38), as did the neutral osmium formyl $OsBr(CHO)(CO)_2(P(C_6H_5)_3)_2$ described by Roper (155).

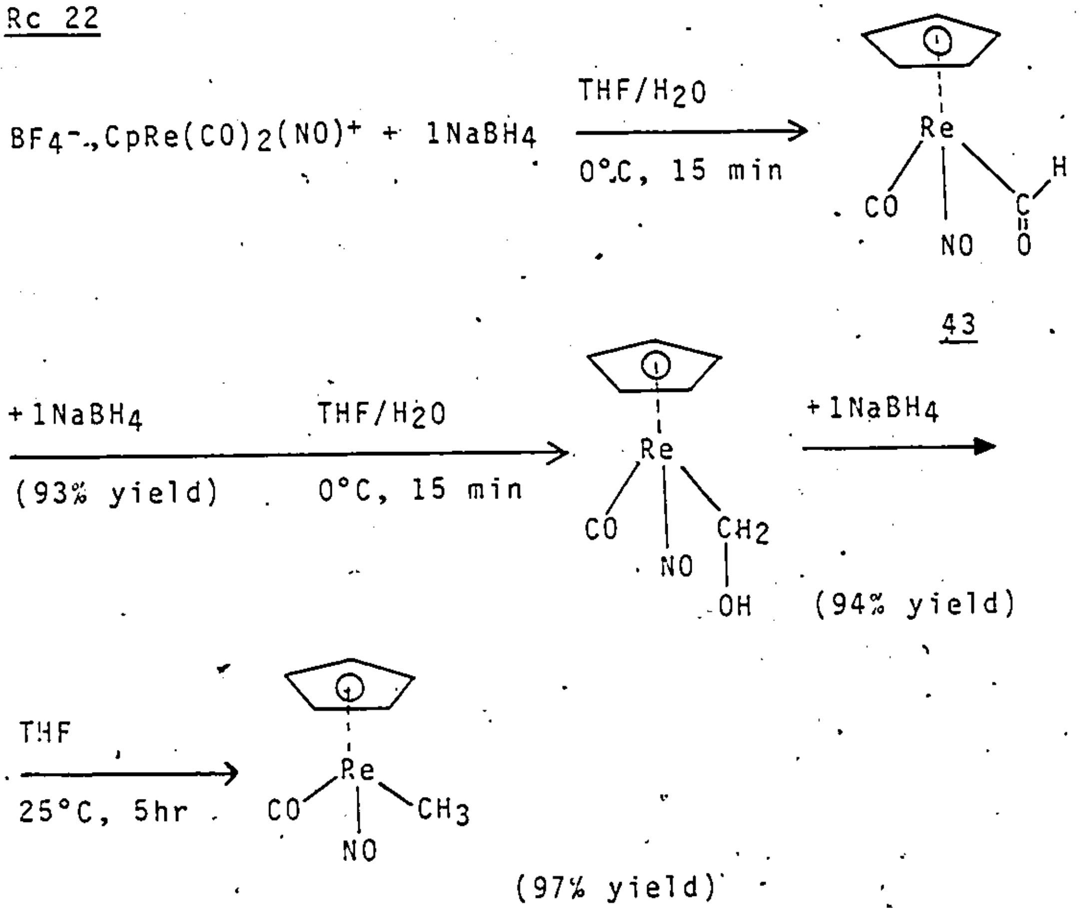
Rc 21

$$((C_5H_6)_3P)_2(CO)_2IrCHO \xrightarrow{-40°C} HIr(CO)_2(P(C_6H_5)_3)_2 + CO$$

Further complications were very likely to arise when the hydride was itself kinetically unstable. In these cases, the formation of a bimetallic dimer accompanied by H_2 evolution was expected to occur (41, 58). As an example, the transient formation of the unstable hydride $HCo(CO)_3(P(C_6H_5)_3)$ was suggested in the reduction of the cobalt cation $[Co(CO)_3(P(C_6H_5)_3)]^+$ with $NaBH_4$ which led to a high yield of the cobalt dimer $[Co(CO)_3(P(C_6H_5)_3]_2$ (149).

Prior to decomposition, some formyl complexes are known to undergo further reaction with additional reducing equivalents yielding a variety of products (depending on which electrophilic center in the complex is the site of the reduction (-CO or -CHO)). Recently, the sequential polyreduction depicted in Rc 22 was reported (156) by treatment of the rhenium cation 42 with sodium borohydride. It was the first instance in which models for all presumed Fischer Tropsch stages were isolated.

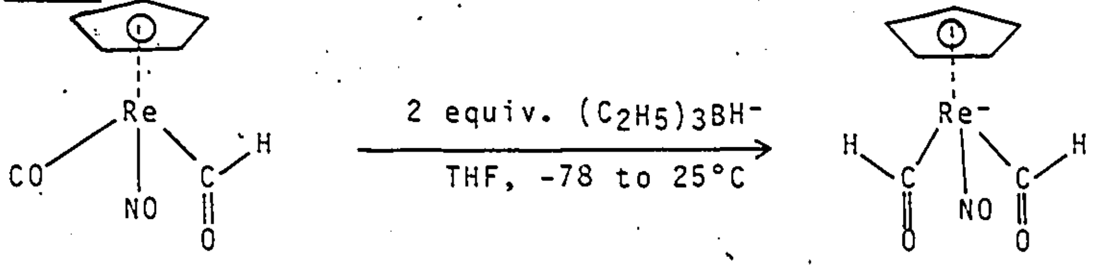
Rc 22



45

Furthermore, treatment of the rhenium complex 43 with one equivalent of $(C_2H_5)_3BH^-,Li^+$ yielded the diformyl metal complex 46 (157) depicted in Rc 23.

Rc 23

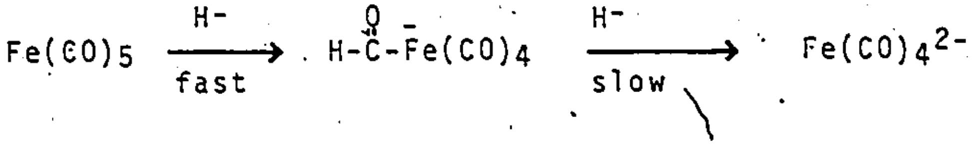


43

46

Alternatively, the reduction can lead to the generation of metalates. This has been demonstrated by Rc 24. $Fe(CO)_5$ reacted with 2.5 equivalents of $(s\text{-}C_4H_9)BH^-,K^+$ at room temperature to afford the analytically pure $K_2Fe(CO)_4$ in 95-100% yield (158).

Rc 24

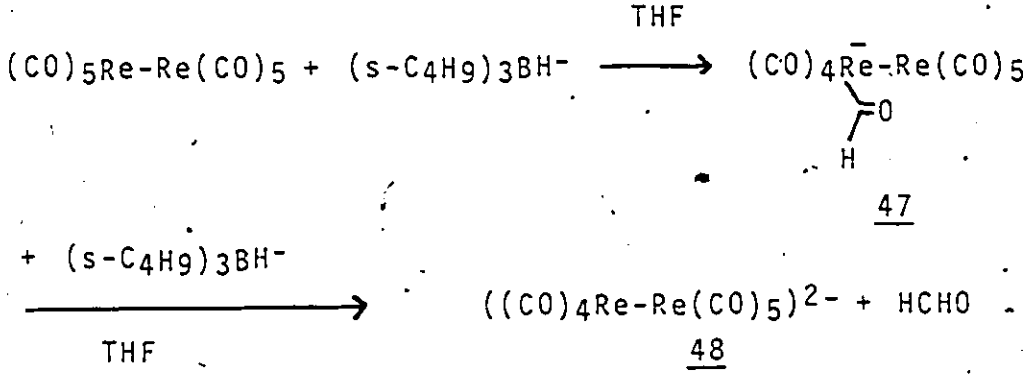


$$Fe(CO)_5 \xrightarrow[\text{fast}]{H^-} H-\overset{O}{C}-\bar{Fe}(CO)_4 \xrightarrow[\text{slow}]{H^-} Fe(CO)_4{}^{2-}$$

The reaction proceeded via a rapidly formed metal formyl intermediate.

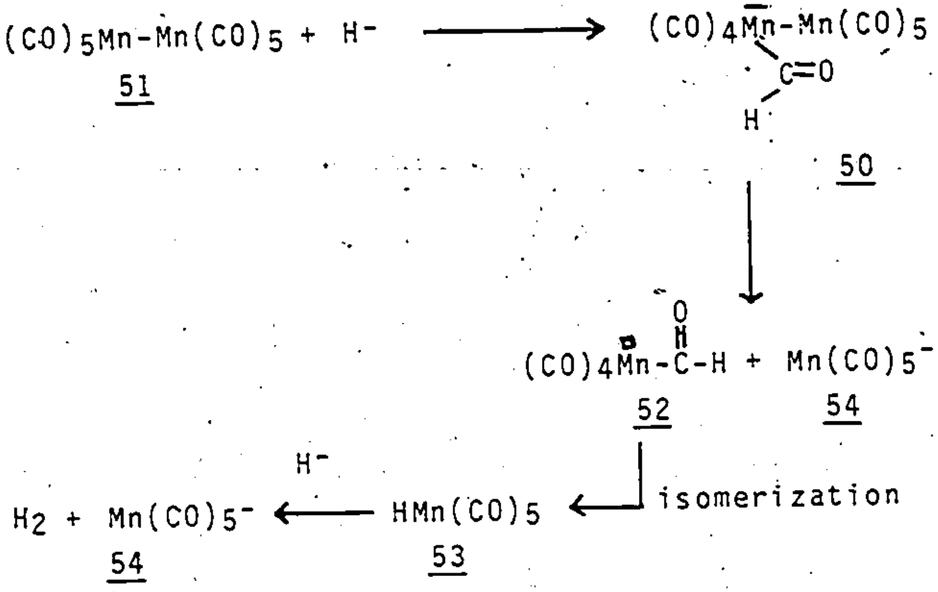
Similarly, the bimetallic dianion 48 was obtained by reacting the binuclear formyl complex 47 with excess reducing agent (159), as shown in Rc 25.

Rc 25



It is worth noting the stability of the dirhenium formyl 47 with respect to metal-metal bond cleavage. Contrary to 47, the structurally related dimer $Mn_2(CO)_{10}$ 51 (Rc 26) underwent metal-metal bond cleavage when reacted under the same conditions (160). It is believed that the reaction proceeds as illustrated in Rc 26.

Rc 26



The fast reduction of the manganese hydride 53 into the manganese anion 54 has been verified independantly (161).

The reaction depicted in Rc 26 was shown to be of preparative value in the synthesis of a variety of metal carbonylated mono anions when extended to other bimetallic dimers (160, 162, 163).

These formyl complexes are attractive compounds for at least two reasons:

1) their relevance to model Fischer-Tropsch chemistry;

2) their ability to be converted into metal hydrides or metallic anions.

A second preparative route to nitrosyl iron hydrides (and the related aryldiazonium (164, 165)) to be explored was the reduction of iron nitrosyl cation.

Since the cation $[Fe(CO)_2(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ 9 was readily available from anion 1 (Chapter I), a study on the reaction of this complex with reducing agents was undertaken.

Results and Discussion

Since the reducing agent $(CH_3CH_2)_3BH^-,Li^+$ was available as a one molar THF solution, the reduction were carried out initially in THF as solvent (see the reaction scheme VI, page 96). Addition of one to three equivalents of reducing agent 55 on a suspension of cation 9 $[(P(C_6H_5)_3)_2Fe(CO)_2(NO)]^+BF_4^-$ in THF resulted in decomposition products. Cation 9, suspended in THF, reacted very slowly at temperatures below -20°C but within 15 minutes in the temperature range -20 to 0°C. Once the reaction was completed, the homogeneous dark green reaction mixture was examined by ^{31}P NMR, IR (table VI, page 97), and by thin layer chromatography. Free triphenylphosphine and a mixture of iron dinitrosyl $Fe(NO)_2(P(C_6H_5)_3)_2$ 6 and iron carbonyl complexes $Fe(CO)_4(P(C_6H_5)_3)$ 7 and a small amount of $Fe(CO)_3=(P(C_6H_5)_3)_2$ 8 were detected (this mixture of decomposition products will be referred thereafter as degradation products).

The course of the reaction was drastically altered when an excess of the reducing agent 55 (∿ 6 equivalents) was used. Now the lithium salt of anion 57 $(P(C_6H_5)_3)Fe(CO)_2NO^-$ was the only iron containing product to be detected by infrared or ^{31}P NMR (table VI) of the orange solution. A spectroscopic yield of approximately 80% was obtained (explanation of spectroscopic yield in the experimental section). There was no indication, either by IR or ^{31}P NMR, of any formation of the anion 58 $(P(C_6H_5)_3)_2Fe(CO)(NO)^-,Li^+$. The lithium salt of anion 58 was generated independantly by adding 55 to a stirred solution of hydride 4 in THF at room temperature. After stirring for one hour a single peak at = 81.4ppm was detected in the ^{31}P NMR spectrum of the red solution. On passing CO through the solution, the red colour gradually changed to yellow within a few minutes. The infrared and ^{31}P NMR spectra were in agreement with the formation of anion 57. This offers an alternate synthesis of a solution of anion 57 with a known concentration.

A third route to 57 involved the reduction of the iron nitrosyl hydride 3 (prepared according to Rc 4, chapter I). Addition of the reducing agent 55 (1.2 equivalent) to a solution of hydride 3 in ether at 0°C resulted in the rapid conversion (5 minutes) into the anion 57.

The lithium salt of anion 57 could also be generated by slow addition (at room temperature) of the cation 9, dissolved in methylene chloride, to six equivalents of the reducing agent 55 (in THF). Inverting the order of addition (addition of hydridic reagent 55 to cation 9) resulted once again in the formation of the degradation products. Trace of anion 57 was also detected by infrared in this case.

To rationalize these observations, a simple model could be developed when it was observed that the anion 57 (generated from 4 with one equivalent of 55) reacted almost instantaneously in THF at 0°C with cation 9 added as a solid. The same mixture (based on IR spectra of the solutions) of degradation products 6, 7, and 8 was obtained as in the direct reduction of cation 9 with less than 3 equivalents of 55. This formation of the degradation products suggested again that the decomposition reaction must proceed via a bimetallic intermediate. Indeed in similar reactions closely related to the iron nitrosyl cation 9 and the anion 57 by the NO displacement rule (78), such as in the reaction of cobalt cations with cobalt anions (166), yielded stable metallic dimers.

However, as detailed in chapter I, extensive nitrosyl and carbonyl transfer reactions occur once the iron nitrosyl dimer is formed, unlike most cobalt dimers.

The effect of excess hydride on the products distribution can be rationalized upon considering the demonstrated property of the boron hydride 55 to reductively cleave metal-metal bonds which is known to yield monometallic anions (160). As the reaction proceeded, anion 57 and cation 9 being in contact led to the formation of the bimetallic complex (scheme VI; page 96) $(P(C_6H_5)_3)_x(NO)(CO)_2Fe\text{-}Fe(CO)_2(NO)(P(C_6H_5)_3)_y$ $(x+y \leq 4)$ 59. As the amount of reducing agent 55 is progressively increased, the reductive cleavage of the iron-iron bond in the bimetallic complex 59 is expected to compete progressively more efficiently with nitrosyl and carbonyl transfer reactions (leading to the degradation products). Indeed this is what was actually observed. On going from 3 to 6 equivalents of reducing agent 55, an increasing amount of 57 was produced to the point where it was the only product to be formed (on the basis of IR and ^{31}P analysis).

In an attempt to identify at least one of the primary processes implicated in the reaction of 9 with H-, the reduction was done directly in the NMR tube (in CH_2Cl_2) at low temperature by mixing cation 9 with a limited amount of the reducing agent 55 (55/9 = 1.5; temperature of mixing was maintained at -70°C). The ^1H NMR showed conclusively the formation of the formyl complex $(P(C_6H_5)_3)_2(NO)(CO)FeCHO$ 56. The low field triplet (δ = 13.5 ppm; J(P-H)= 10 Hz) is the diagnostic of a formyl proton coupled to two equivalent phosphorous nuclei (150). ^1H NMR did not reveal any proton resonance which could be assigned to hydride 3. The proton NMR data were very similar to those of the iridium formyl complex $(P(C_6H_5)_3)_2(CO)_2Ir-CHO$ (δ = 12.85 ppm, J(P-H)= 17 Hz) recently reported in the literature (38).

The evolution of these reactions is more conveniently monitored by ^{31}P NMR which indicated for the formyl 56 : δ ^{31}P = +64.3 ± 0.2 ppm (external lock on D_2O, 85% H_3PO_4). The measurement of the peaks' intensity for cation 9 and formyl 56 indicated their presence in the reaction solution in a ratio of 56/9 = 3 (Low temperature NMR).

This may suggest an equilibrium between 9 and 56 (9 + 55 $\rightleftharpoons$ 56) as noted previously in other cases (62) or a partial conversion of 9 to 56 (9 + 55 $\longrightarrow$ 56). Analysis of the case favored an equilibrium between 9 and 56. The formyl complex 56, particularly unstable, decomposed rapidly above -30°C into the degradation products (infrared of the reaction solution). If a partial reaction occurred (9 + 55 $\longrightarrow$ 56), 1.5-0.75 = 0.75 equiv. of unreacted 55 is still available (1.5 equiv. of 55 initially; after reaction 0.75 equiv. of 56 and 0.25 equiv. of 9), which will react with water, if any present, to give OH^-. This 0.75 equiv. of OH^- can now react with hydride 3 (from the decomposition of 56) to form 0.75 equiv. of the anion 57 where 0.25 equiv. of which would react with the available 0.25 equiv. of cation 9, affording the degradation products. Hence, this reasoning would imply that 0.75 - 0.25 = 0.50 equiv. of undecomposed anion 57 is still present in solution. But no trace of anion 57 was detected by IR and ^{31}P NMR of the reaction solution at the end of the reaction. One may go further and assume that exactly 0.25 equiv. of OH^- was produced (not more, not less) leading to the detection of the degradation products only. But this hypothesis is very unlikely.

From this deductive reasoning, it was concluded that the hypothesis of an equilibrium between 9 and 56 was the most valid.

Thus 55 was still available to react with any hydride 3 which could have precluded its detection in the ^{1}H NMR experiment. Indeed as the decomposition of 56 (-40 to - 30°C) proceeded towards the formation of the degradation products, anion 57 (on the basis of δ values) was detected as a transient intermediate, thus suggesting that a reaction between 9 and 57 was still possible even if 55 was present in minimal amount.

Based on the ability of hydride 3 to react very rapidly with the reducing reagent 55 and on the demonstrated tendency of formyl complexes to isomerize into hydrides, which when kinetically unstable are known to decompose via a bimetallic intermediate, one of the primary processes (if not the only reaction mechanism) is very likely to be the following (scheme VI). On the addition of an excess of reducing agent 55, the formyl complex 56 is formed which isomerized into the known nitrosyl hydride 3 and is subsequently reduced into anion 57. Anion 57 may react with unreacted cation 9 to give the unstable bimetallic complex 59. But in the presence of an excess of 55, the bimetallic 59 is reductively cleaved to give the anion 57 again. In the absence of an excess of reducing agent 55, the bimetallic 59 (under certain conditions hydride 3 also) will decompose into the degradation products 6, 7 and 8.

In summary, the new features investigated in the above system are:

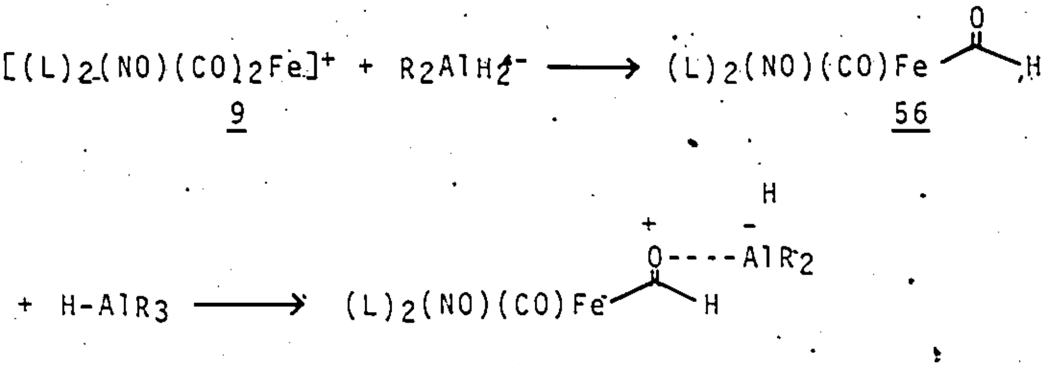
(a) As it was detailed in the introduction, a formyl, or a hydride or a metallic dimer can be formed (depending on the kinetic stability of the reaction intermediate) in the reaction of metallic cations with an equivalent amount of reducing agents. To the best of our knowledge, there is no previous work reporting the formation of an unstable dimer in similar reductive reactions.

We also recognized that the formation of metallic dimers can occur by other routes than the decomposition of hydrides such as the fast reaction of the starting material (cation 9) with the reaction product (anion 57).

(b) In all of the previously reported examples of reductive reactions with excess reducing agents (reaction that does not involve reductive cleavage of a metal-metal bond), metalates were formed with one CO less than the starting material. This was contrary to the present study where the metalate was formed from cation 9 with no CO loss. This result implied that further reduction of the formyl complex was a slow process with respect to its transformation into the hydride.

In order to demonstrate that the polyreduction of one of the carbonyl ligands in the cationic comlex 9 was a feasible process, new strategies which would increase either the stability of the formyl intermediate or the reactivity towards further reduction had to be investigated. Towards this end, it was decided to attempt the polyreduction of cation 9 with a large excess of $R_2AlH_2^-,Na^+$ (Red Al; $R=CH_3$-O-CH_2CH_2-O). It was possible that after the transfer of the first equivalent, R_2AlH could act as a Lewis acid center toward the oxygen atom of the formyl ligand and provide an increase in the formyl stability as illustrated in Rc 27.

Rc 27



$L = P(C_6H_5)_3$

This would bring the second reducing equivalent (the remaining hydride attached to Al) in the near vicinity of the formyl carbon and consequently facilitate the over-reduction of cation 9. A similar approach was used recently by Casey (150), as our work was in progress, by converting in 45% isolated yield the rhenium cation 60a into the hydroxymethyl complex 61a (Rc 28).

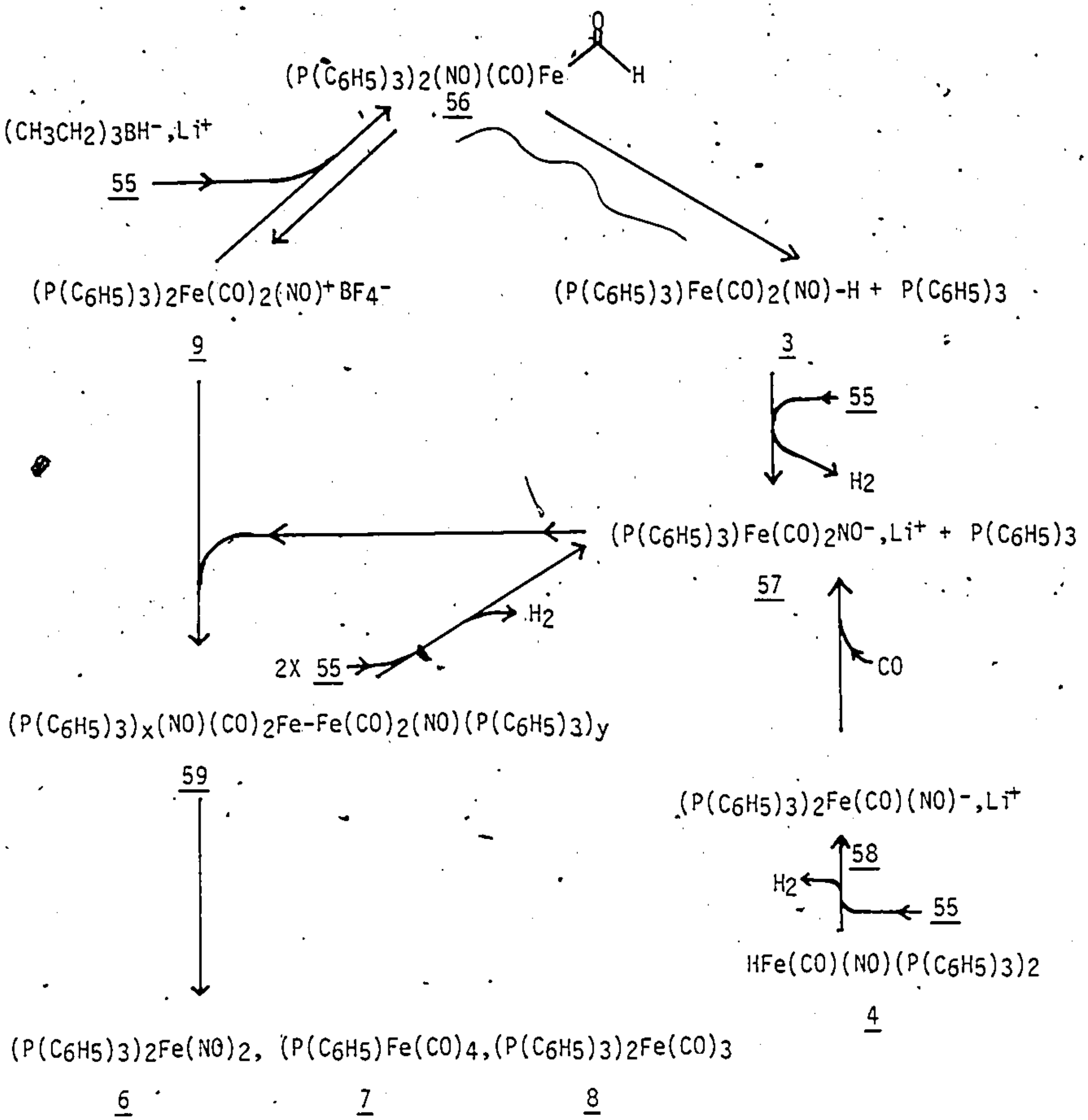
Rc 28

$$\underset{\underline{60a}}{(C_5H_5)Re(CO)_2(NO)^+, PF_6^-} + (CH_3CH_2)_2AlH_2^-, Na^+ \longrightarrow \underset{\underline{61a}}{(C_5H_5)Re(CO)(NO)(CH_2OH)}$$

Also this reasoning was based on the reported observation that $Mo(CO)_6$ was successfully reduced to ethylene with AlH_3 as reducing agent (167). In this study, the author postulated that the complexation of the aluminum (Lewis acid center) on the oxygen of the carbonyl ligand was the key factor in allowing the poly-reduction to occur. Also, attempts with reducing agents of the electrophilic type such as R_3BH^-,Li^+ were unsuccessful (seeking directly electrophilic center).

On addition of an excess of $(CH_3CH_2)_3BH^-,Li^+$ (100 equivalents) on cation 9, only molecular hydrogen was detected by vapor phase chromatography (vpc). However, using $(CH_3\text{-}O\text{-}CH_2\text{-}O)_2AlH_2,Na^+$ instead of the boron hydride led to the generation of a small quantity of hydrocarbons (1% of methane characterized by vpc and mass spectroscopy, $(m/e)^+=16$ and 15 with equal intensity; collaboration with Professor B. Morrow, Ottawa University).

Scheme VI



$x + y \leq 4$; x and y are function of the number of bridging NO and/or CO and on the coordination mode of NO (three or one electron ligand).

Table VI

IR and NMR Data

Complex		ν (CO)	ν (NO)	Solvent[a]	δ ^{31}P [b]
$L_2Fe(CO)(NO)^-,Li^+$	58	1830	Overlapped by solvent absorption		+81.4
$L_2Fe(CO)(NO)^-,Na^+$	58	1830s, 1780w	1540	THF	
$LFe(CO)_2(NO)^-,Li^+$ [c]	57	1920s, 1850s 1895w, 1820w 1895s, 1820s	1530s 1600w 1600w	THF CH_3CN	+78.3
$LFe(CO)_2(NO)^-,Na^+$	57	1920s, 1840s 1900w, 1800w 1895s, 1820s	1570s 1620w 1600s	THF CH_3CN	
$L_2Fe(CO)(NO)(CHO)$	56				+64.3
$LFe(CO)_4$	7	2060, 1975, 1945 2059, 1978, 1958		THF, CH_2Cl_2 $CHCl_3$	+71.5
$L_2Fe(CO)_3$	8	1890		THF, CH_2Cl_2 $CHCl_3$	+83.3
$L_2Fe(NO)_2$	6		1720s, 1670vs 1724s, 1678vs	THF, CH_2Cl_2 nujol	+61.4

$L = P(C_6H_5)_3$

s = strong w = weak

a UNICAM SP 1100 IR apparatus

b external lock on D_2O, δ in ppm (± 0.2 ppm depending on the relative amount of CH_2Cl_2, THF and the temperature) with δ $P(C_6H_5)_3$ = -5.1 ppm relative to external 85% H_3PO_4.

c PERKIN ELMER 287 IR apparatus

APPENDIX

Characterization of Anions

Anion $Fe(CO)_3NO^-,Na^+$ 1 was the only example of an iron carbonyl nitrosyl anion published in the literature for which infrared data were given(108, 50). The synthetic use of $Fe(CO)_2(NO)(P(OC_6H_5)_3)^-,Na^+$ was briefly mentioned in one publication, but no infrared data were given by the author (175). As was the case for anion 1, ion pairing phenomena were observed also for the iron carbonyl nitrosyl anions synthesized in this work. These ion pairing phenomena, which were briefly considered in chapter I, are now discussed in more detail, in order to illustrate the approach used to characterize the new metalates prepared in this work.

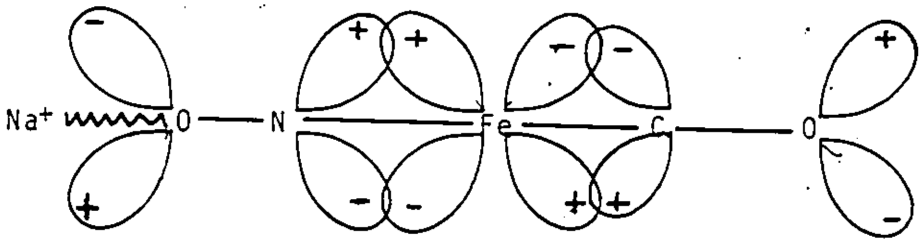
Although ion pairing phenomena have been observed several years ago between alkali metal and the oxygen atom of a terminal ketonic group or carbonyl group for $Co(CO)_4^-$ (168), $Fe(CO)_4(C(O)R)^-$ (169) and others (170, 171), cation-nitrosyl ion pairing was reported for the first time in 1977 by Pannell (93) for anion 1.

The solution infrared spectrum of anion 1 in solvents known to solvate cations efficiently (DMSO, CH_3CN, diglyme) indicated the presence of single species (IR(CH_3CN): νCO 1982 cm^{-1}, 1882 cm^{-1}; ν(NO) 1640 cm^{-1}).

In tetrahydrofuran, a spectrum that was essentially doubled, compared to the one given above, was observed (IR(THF): ν(CO) 1990 and 1977 cm^{-1}, 1890 and 1873 cm^{-1}; ν(NO) 1615 and 1648 cm^{-1}). The gradual addition of a solvent with a high solvating power, such as 18-crown-6 cyclic polyether, diminished the intensity of the high frequency carbonyl bands (1990 and 1890 cm^{-1}) and the low frequency nitrosyl band (1615 cm^{-1}) with a corresponding increase in the intensity of the low carbonyl (1977 and 1873 cm^{-1}) and high nitrosyl (1648 cm^{-1}) bands, until a single pattern was obtained similar to the pattern reported in acetonitrile.

These changes in the IR spectrum, brought about by changing the solvating ability of the solvent, are an indication of the occurence of an equilibrium between tight ion pair species <u>A</u> and solvated ion pair species <u>B</u>

$$\underset{\underline{A}}{(CO)_3FeNO^- \sim\!\sim Na^+} \quad + \quad S \quad \rightleftharpoons \quad \underset{\underline{B}}{(CO)_3FeNO^-(S)Na^+}$$



Furthermore, the trends observed can only be explained by considering a specific interaction of the cation and the nitrosyl's oxygen in the tight ion pair.

As the interactions $Na^{+} \sim\sim\sim ON$ are gaining strength (in solvent of low solvating power) the electronic density is transfered from the $[Fe(CO)_3]^-$ moiety into the NO ligand. The back-bonding $M \rightrightarrows NO$ increases and consequently the NO bond order and the ν (NO) decreases. On the other hand increasing back bonding towards the NO implies decreasing the back bonding towards the CO ligands. Thus the CO bond order and ν (CO) increases as observed.

We had independantly undertaken the same study (172) prior to the publication of Pannell's paper. An additional observation was made since the infrared spectra were recorded in ether (data in ether were not given by Pannell). These spectra showed that the ν (CO) and ν (NO) of the contact ion pairs in ether (ν CO=1995, 1905 cm^{-1}, ν NO= 1985 cm^{-1}) are respectively higher and lower than those of the contact ion pairs in THF. This implied a stronger interaction (see table page 110) of the cation with the nitrosyl ligand in ether than in THF. Considerable aggregation of the ion pairs is suspected to occur (93) and it is possible also that the state of aggregation of the contact ion pairs in ether compared to those in THF are indeed different.

The identification of anionic species in solution is complicated severely by the occurrence of ion pairing phenomena. For example, in the case of $Fe(CO)_3NO^-,Na^+$, a C_{3v} symmetry for the three carbonyls would give a theoretical spectrum indicating two absorptions from the carbonyl ligands (one being degenerate) and one nitrosyl absorption. However, the infrared spectrum in THF indicated four carbonyls and one nitrosyl absorption which is totally incompatible with the given structure. Thus when infrared spectroscopy of an anionic specie reveals more vibrations than predicted, in order to formulate a structure, it is necessary to investigate the modifications in the spectrum resulting from a change in the solvent and/or by transforming the species into known compounds.

These principles have been followed in order to characterize the new anionic nitrosyl derivatives containing triphenylphosphine as one of the ligands, prepared in this work.

The ion pairing phenomena occurring for anion <u>1</u>, were observed also for the sodium (prepared using sodium amalgam) and lithium salt (prepared using lithium boron hydrides) of the anion $Fe(CO)_2(NO)(P(C_6H_5)_3)^-$ <u>57</u> and possibly for the anion $Fe(CO)(NO)(P(C_6H_5)_3)_2^-$ <u>58</u>.

The solution infrared spectrum of the sodium salt of anion 57, as was the case for anion 1, indicated the presence of single species in acetonitrile. (IR (CH_3CN): ν (CO) 1900 cm^{-1}, 1825 cm^{-1}; ν (NO)=1600 cm^{-1}). In tetrahydrofuran, the infrared spectrum was essentially doubled compared to that above (IR (THF): ν (CO) 1910 and 1890 cm^{-1}, 1840 and 1800 cm^{-1}; ν(NO) 1560 and 1620 cm^{-1}. However more tight ion pair species were present in solution than the solvated ion pair species by an approximate ratio of 2:1. Addition of acetonitrile and then subjecting the system to vacuum to re-establish the original concentration, gave the same infrared spectrum obtained in "pure" acetonitrile. Since acetonitrile removed the cation from a tight ion pairing situation, the data indicated the presence of two species, tight ion pairs A and solvent separated ion pairs B in equilibrium as shown below.

$$(P(C_6H_5)_3)Fe(CO)_2NO^-,Na^+ \rightleftharpoons (P(C_6H_5)_3)Fe(CO)_2NO^-(S),Na^+$$

A B

It is apparent that ion pairs A involve a cation nitrosyl interaction since removal of the cation from this environment by adding acetonitrile caused an increase in the ν (NO) and a decrease in the ν (CO's), as observed for anion 1.

The infrared spectrum of the anion 58 $(P(C_6H_5)_3)_2$= $Fe(CO)(NO)^-$,Na^+, in THF, again showed a spectrum which was essentially doubled with high intensity bands of tight ion pair species at 1830 cm^{-1} (ν (CO)) and 1540 cm^{-1} (ν (NO)) and very low intensity bands at 1780 cm^{-1} (ν(CO)) and 1595 cm^{-1} (ν (NO)) for might be those of the solvent separated ion pair species. Unfortunately, the ion pairing phenomena could not be fully studied for anion 58, because of its extreme sensitivity to oxygen.

The same ion pairing phenomena was observed for the sodium salt of the anion $Fe(CO)_2(NO)(P(OC_6H_5)_3)^-$ having a spectrum which was essentially doubled, indicating the presence of tight and separated ion pair species in solution. (IR(THF); ν (CO): 1950 cm^{-1} and 1875 cm^{-1} strong, 1930 cm^{-1} and 1845 cm^{-1} weak; ν (NO): 1600 cm^{-1} strong and 1655 cm^{-1} weak. Again, the ion pairing phenomena could not be studied due to the air sensitivity of the anion.

The Li^+ salt of anion 57 and anion 58 exhibited similar behaviour to that of the Na^+ counter cation, but with a greater amount of tight ion pairing species compared to the Na^+ salt. Furthermore, in anion 57 the stretching frequency of the carbonyls was shifted to higher value by 10 cm^{-1} and the nitrosyl stretching frequency to lower values by 10 to 20 cm^{-1} as illustrated in Table VII.

Table VII

IR DATA of $Fe(CO)_2(NO)(P(C_6H_5)_3)^-$ 57

Cation	νCO_1		νCO_2		νNO	
	A	B	A	B	A	B
Na^+	1920	1900	1840	1800	1560	1620
Li^+	1920	1900	1850	1825	1540	1610

A = high intensity absorption band (tight ion pairs)

B = low intensity absorption band (separated ion pairs)

ν in cm^{-1}; solvent = THF

Such a shift in the stretching frequencies can be explained by the fact that the smaller, less polarized cation Li^+ has a greater interaction with the oxygen of the nitrosyl ligand ($Li^+ \sim\sim\sim O-N-Fe-C-O$).

A similar trend was observed by Collman (95) for the complex $[RC(O)Fe(CO)_4]^-$. It was anticipated that the acyl group was the cation binding site. Consistent with this reasoning, the acyl stretching frequency shifted to lower values with smaller, less polarized cations $PPN^+ \longrightarrow Na^+ \rightarrow Li^+$). Similarly, with the iron nitrosyl anions, the greater alkali metal nitrosyl interaction exhibited by Li^+ resulted in an increase in nitrogen π back bonding and caused a greater decrease in the nitrosyl stretching frequency. This increase in M-NO π bonding resulted in a decrease of electron density on the metal, thereby decreasing M-CO π bonding with a resulting increase in the carbonyls stretching frequencies.

Comparing the stretching frequencies of the anions $Fe(CO)_3NO^-$, $P(OC_6H_5)_3Fe(CO)_2(NO)^-$ $P(C_6H_5)_3Fe(CO)_2NO^-$, $(P(C_6H_5)_3)_2Fe(CO)(NO)^-$, a gradual decrease in the frequencies was observed.

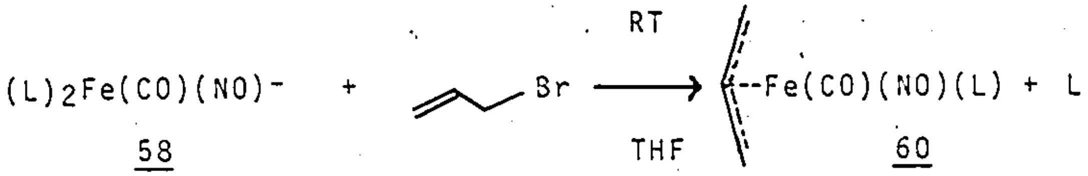
It has been known for some time that replacement of one or more CO ligands of a transition metal carbonyl complex with a tertiary phosphorus ligand caused the stretching frequencies of the remaining carbonyls to fall by an amount which depended on the number and nature of the phosphorous ligands (173, 174). The carbonyl group is a strong π acceptor and triphenylphosphite is a stronger πacceptor than triphenylphosphine but weaker than the carbonyl ligand. Hence, replacement of a carbonyl group with other ligands such as tertiary phosphine ligands will increase the electronic density on the central metal atom (depending on the σ basicity of the ligand) which will drift in the π * orbital of the carbonyl groups (back bonding) and consequently decreasing the bond order and ν (CO).

Tertiary phosphine ligands (which are better σ donors and poorer back-bonders than CO ligand) are also known to increase the basicity on the metal and consequently the nucleophilicity of metallic anions (155).

According to the structure proposed for anion <u>57</u> and <u>58</u>, an increase in reactivity towards formation of the corresponding π allyl (on reacting with allyl halides) should be observed with increasing numbers of triphenylphosphine ligands coordinated on the complex.

Indeed, addition of allyl bromide to anion <u>58</u> in THF (generated either with Na/Hg amalgam or with $Li(C_2H_5)_3BH$) reacted instantaneously at room temperature to give π allyl <u>60</u> (176) as shown in Rc 28.

<u>Rc 28</u>

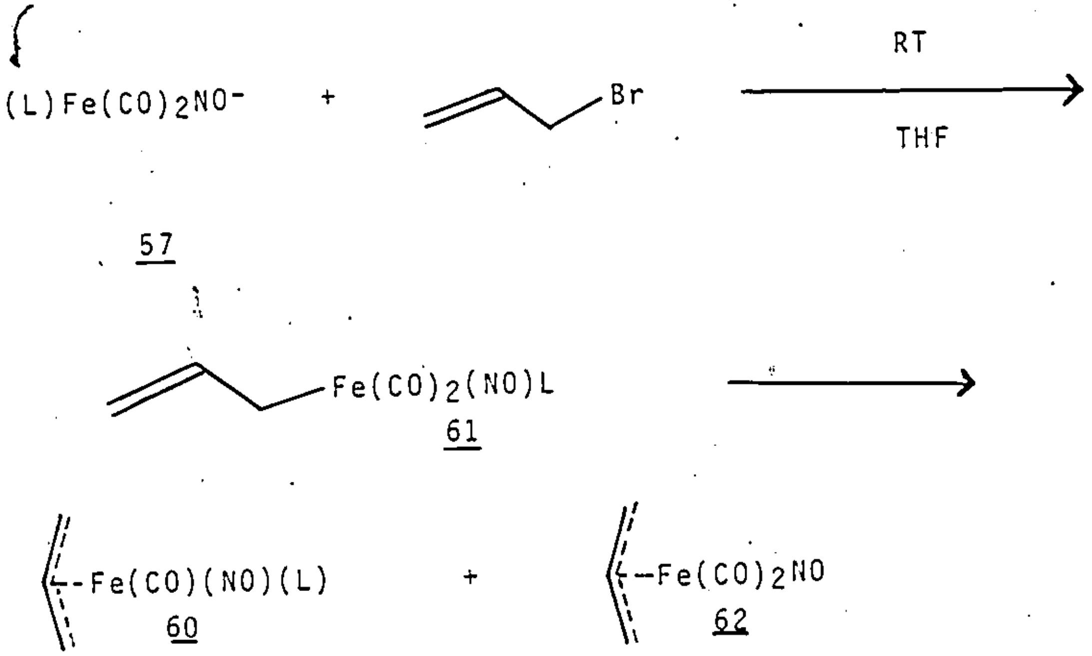


$L = P(C_6H_5)_3$

<u>60</u> was obtained as a red crystalline material in 63% yield, after chromatography on alumina.

Similarly, addition of allyl bromide on anion 57 (prepared either with Na/Hg amalgam or with $Li(C_2H_5)_3BH$) afforded a 3:5 (based on IR absorption intensities) mixture of π allyl 60 and π allyl 62 (177) (Rc 29) after stirring for 15 hours. The reaction pathway is believed to involve a σ allyl intermediate 61, based on IR monitoring of the reaction solution (νCO = 2010, 1950 cm^{-1}; νNO = 1740 cm^{-1}). This intermediate was formed instantaneously on addition of the allyl bromide and evolved gradually (hours) to give a mixture of π allyl 60 and 62.

Rc 29



$L = P(C_6H_5)_3$

Table VIII depicts the observed trend in the reaction time to form the corresponding π allyls, starting from iron nitrosyl anions containing 0 to 3 coordinated triphenylphosphines.

Table VIII

Complex	Reaction time for completion	Products
$Fe(CO)_3NO^-$	24 hrs	$C_3H_5Fe(CO)_2NO$
$(P(C_6H_5)_3)Fe(CO)_2NO^-$	15 hrs	$C_3H_5Fe(CO)_2NO$ + $C_3H_5Fe(CO)(NO)(P(C_6H_5)_3)$
$(P(C_6H_5)_3)_2Fe(CO)NO^-$	fast (sec)	$C_3H_5Fe(CO)(NO)(P(C_6H_5)_3)$

These conversions with allyl bromide to yield the corresponding π allyl together with the spectroscopic properties given earlier have enabled a clear identification of anion <u>57</u> and <u>58</u>.

Table IX

Infrared Data

Complex	ν (CO)(cm^{-1})	ν (NO)(cm^{-1})	Solvent
$Fe(CO)_3NO^-, Na^+$ 1	1990, 1977, 1890, 1873 1990, 1880 1995, 1905vs	1615, 1648 1650 1585	THF CH_3CN ether
$Fe(CO)_2NO(L)^-, Na^+$ 57	1920, 1900(w) 1840, 1800(w) 1895, 1820	1620(w), 1570 1600	THF CH_3CN ether
$Fe(CO)(NO)(L)_2^-, Na^+$ 58	1830, 1780(w)	1540	THF
$Fe(CO)_2(NO)(L)$  61	2010, 1950	1740	THF
$C_3H_5Fe(CO)_2NO$ 62	2030, 1980	1750	THF
$C_3H_5Fe(CO)(NO)L$ 60	1940	1700	THF

ν = Strong in all cases except when indicated otherwise.

L= $P(C_6H_5)_3$

CHAPTER IV

EXPERIMENTAL

1. Apparatus and Materials

All the operations were done in argon or in vacuo. THF (tetrahydrofuran) was refluxed, then distilled from sodium/benzophenone under nitrogen and used immediately. Methylene chloride and acetonitrile were refluxed and distilled over phosphorous pentoxide under argon. These were stored under argon over molecular sieves 4A. All the solvents were saturated with argon before use. Anhydrous ether (Mallinkrodt) triphenylphosphine (Aldrich 99%), $Fe(CO)_5$ (Pressure Chemical), $Na^+NO_2^-$ (B.D.H.), acetic anhydride (Ac_2O, J.T. Baker), CF_3COOH (MCIB or J.T. Baker), aqueous 37% HBF_4 (Applied Chemicals) CO, (Matheson, CO C.P. 99.5% min.) were used as received. Lithium triethyl borohydride (1M in THF) and sodium bis (2-methoxyethoxy) aluminum hydride (3.5M in benzene) (Aldrich) were also used as received. Silica gel plates for analytical chromatography were obtained from Analtech, Inc. IR spectra were recorded on a UNICAM SP 1100 calibrated with a polystyrene film or on a Perkin Elmer 283.

NMR spectra were recorded on a Varian HA 100 for protons (TMS internal reference) and on a Varian FT 80 operating at 32.2 MHz for phosphorus (85% H_3PO_4 external reference); a positive chemical shift indicates a resonance downfield from the reference. Elemental analysis were performed by Chemalytics Inc., Tempe Arizona or M.H.W. Laboratories, Phoenix, Arizona U.S.A.

2. Preparation of sodium tricarbonylnitrosyferrate $NaFe(CO)_3NO$ 1

The preparation was taken from reference (74) with changes to the work up procedure. The reaction system consisted of a three-necked flask provided with a rubber septum, a reflux condenser attached to a mercury bubbler, and a stopcock attached to an argon inlet.

$NaNO_2$ (5.2g) was dissolved in methanol (270 ml), then sodium (4.0g) was added in small pieces. After dissolution, $Fe(CO)_5$ (10.0 ml) was added and the system refluxed at 70°C for one hour.

After the addition of $Fe(CO)_5$ a light orange colour appeared which intensified with time to finally give, after 20 minutes, a brown solution and after one hour, net deposition of a brownish precipitate. Then the methanol was removed by subjecting the system to vacuum at 40°C and the solid residue was kept under vacuum at least 24 hours at room temperature to ensure maximum dryness. The resultant brownish red mass was extracted with ether and the filtered solution concentrated under vacuum at 0°C until few crystals appeared. Further cooling to -10°C with addition of small amounts of hexane (or benzene) and occasional swirling afforded most of the compound in the solid state. The solid was separated from the slightly colored solution, washed with hexane and benzene and dried under vacuum (3 hours) (yield: 14g, 99%).

The solid retained approximately one mole of methanol as a solvate per mole of anion (NMR of a CD_3COCD_3 solution calibrated with a known amount of toluene). It was taken into account in calculating the amount of <u>1</u> used. The compound was known to form solvates with dioxane (74) and acetone (90). It was stored under argon at 0°C, because of its sensitivity to water, oxygen and light. After several months the yellow color slightly turned green, possibly due to some oxidation. Hydride <u>3</u> and <u>4</u> could also be prepared with the slightly oxidized anion.

3. $HFe(CO)(NO)(P(C_6H_5)_3)_2$ <u>4</u>:

Trifluoroacetic acid (0.52 ml, 0.8 g, 7 mmoles, 1.5 equivalent) diluted with ether (diethyl ether) (10 ml) was added dropwise with a syringe to a stirred ice cold solution of $Fe(CO)_3NO^-,Na^+$ (1.04g, 4.6 mmoles) and triphenylphosphine (7.1g, 27 mmoles, ∿ 6 equivalents) in 175 ml of ether in a three necked round bottom flask. Once the addition was completed, the ice bath was removed and stirring was maintained until gas evolution was no longer observed (∿ 2 hours). (The orange hydride precipitated gradually as a mixture with sodium trifluoroacetate and with concurent evolution of carbon monoxide). After 2 hours, the reaction mixture was cooled and the solid was filtered, washed with 3x10ml of cold ether, and dried under vacuum to remove any trace of trifluoroacetic acid (a small amount of hydride <u>4</u> dissolved in ether, but was not recovered). The hydride was extracted selectively with benzene with which it formed solvates. The extracted solution was reduced under vacuum at room temperature until a few crystals appeared. Cooling of the crystallization solution followed by addition of ether/pentane afforded hydride 4, as a microcrystalline orange powder. The product was filtered, washed with pentane and dried in vacuo. The yield of the orange microcrystalline material was 2.3g, 70%. The hydride is soluble in solvents such as THF, benzene, methylene chloride and is air stable in the solid state for several weeks. Desolution of the solvate molecule of benzene occurred at room temperature when the solid was kept under high vacuum of a mass spectrometer. The mass spectra were not very informative. Ionized iron containing fragments could be detected only at temperatures above 120°C when thermal decomposition of hydride 4 was occurring.

Anal. Calcd. for $C_{37}H_{31}FeNO_2P_2,C_6H_6$: C,72.0; H,5.2; N,1.9. Found: C,71.9; H,5.2; N,1.6.

IR(THF); ν(CO) : 1910 (s) cm^{-1}
ν(NO) : 1690 (s) cm^{-1}

^1H NMR : TMS internal reference, solvent C_6D_6 (37°C), δ H aromatic : complex multiplet (J = 79 ± 1Hz) between 7 and 8 ppm,

δ H-Fe : -5 ppm, triplet J(P-H) = 80 + 2 Hz.

^{31}P NMR : reference 85% H_3PO_4 placed in a coaxial tube, solvent C_6D_6, δP : +77 ppm, doublet J(P-H) = 80 Hz.

4. General procedure for the identification of the degradation products 6, 7, 8, 10, 12:

They were identified by their characteristic infra red spectra, $(Fe(NO)_2(CO)_u(P(C_6H_5)_3)_v$ $(u = 0,1,2;\ u+v=2)$ (178), $(P(C_6H_5))_xFe(CO)_y$ $(x = 1,2;\ x+y = 5)$ 179 and by analytical thin layer chromatography (SiO_2, hexane/benzene = 3/1) for the compounds containing a phosphine ligand. $(P(C_6H_5)_3)Fe(CO)_4$ 7 (180) and $(P(C_6H_5)_3)_2Fe(CO)_3$ 8 (179) were already in hand.

Thermal degradation of the cation $[P(C_6H_5)_3]_2Fe(CO)=(NO)(CH_3CN)^+BF_4^-$ (33) in acetonitrile at 50°C afforded $(P(C_6H_5)_3)_2Fe(NO)_2$ 6 which crystallized out.

Solutions of $(P(C_6H_5))Fe(CO)(NO)_2$ 12 contaminated with a trace amount of 6 were obtained from the reaction of $Fe(CO)_2(NO)_2$ 10 with excess $(P(C_6H_5)_3$ in ether or hexane. On the TLC plates the Rf values of 7 and 16 were found to be very similar, as were those of 8 and 6.

5. Thermal decomposition of hydride 4 in THF:

A solution of 0.5 g of 4 in 30 ml of THF was heated at reflux under argon. Samples were periodically withdrawn for IR analysis. After 4 hours hydride 4 was no longer present. The CO and/or NO containing products consisted mainly of $(P(C_6H_5)_3)_2Fe(NO)_2$ 6, $(P(C_6H_5)_3)_2$=$Fe(CO)_3$ 8 and a small amount of $(P(C_6H_5)_3)Fe(CO)_4$ 7. relative to 8 (as judged from the relative intensities of the ν CO of 7 and 8) $(P(C_6H_5)_3)Fe(CO)(NO)_2$ 12 was not detected. The formation of these compounds was further confirmed by a TLC analysis of the mixture.

6. Preparation of $[Fe(CO)_2(NO)(P(C_6H_5)_3)]_2$ Hg 14

The preparation was taken from reference (82). A solution of $Hg(CN)_2$ (0.67g, 2.7 mmoles) in oxygen free distilled H_2O (10 ml) was added dropwise to a stirred ice cold solution of $Fe(CO)_3NO^-,Na^+$ (1g, 5.2 mmoles) in oxygen free distilled H_2O (50 ml), under the absence of light. Once the addition was completed, the reaction mixture was stirred for an additional 30 minutes at 0°C. The yellow precipitate formed was extracted with methylene chloride (red solution). On evaporation of the solvent under vacuum, red crystals of <u>13</u>, were obtained. These crystals were dissolved in benzene and triphenylphosphine (1.8 g, 6.8 mmoles) was added. Upon stirring, the solution for several hours at room temperature, a fine yellow-orange precipitate gradually formed. After 20 hours this precipitate was filtered, washed with minimum amount of methylene chloride and dried in vacuo to give 1.62 g (63% yield) of $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$. The relatively stable compound is sparingly soluble in organic solvents.

IR (CH_2Cl_2) ; ν (CO) (cm^{-1}) : 1990 (w) , 1960 (m)
ν (NO) (cm^{-1}) : 1720 (s)

7. Reduction of $Hg[Fe(CO)_2(NO)(P(C_6H_5)_3)]_2$ with Na/Hg amalgam (generation of $NaFe(CO)_2(NO)(P(C_6H_5)_3)$

$Hg[Fe(CO)_2(NO)(P(C_6H_5)_3)]_2$ (0.40 g; 0.39 mmol) was added portionwise to a stirred 100% excess Na/Hg amalgam in THF (30 ml). The reaction mixture was stirred at room temperature for 2 hours. Upon filtration of the reaction mixture, a yellow homogeneous solution of the air sensitive anion $NaFe(CO)_2(NO)(P(C_6H_5)_3)$ was obtained.

IR (THF) ; ν (CO) (cm^{-1}) : 1920(s) , 1900(w) ,
1840(s) , 1800 (w)
ν (NO)(cm^{-1}) : 1620(w) , 1570(s)

8. Preparation of $H\text{-}Fe(CO)(NO)(P(C_6H_5)_3)_2$ 4 from Na $Fe(CO)2(NO)(P(C_6H_5)_3)$

Trifluoroacetic acid (0.06 ml, 0.71 mmole) diluted with THF (5 ml) was added dropwise to a stirred solution of $NaFe(CO)_2(NO)(P(C_6H_5)_3)$ (from the Na/Hg reduction of 0.59 mmole of $Hg(Fe(CO)_2(P(C_6H_5)_3))_2$) and 1.6 g (5.9 mmoles) of $P(C_6H_5)_3$ in THF (30 ml) at room temperature. The reaction mixture was stirred for an additional 5 minutes. The volume of the solution was reduced under vacuum until a slight crystallization was evident. The mixture was cooled to 0°C and the crystallization was completed by addition of pentane and the solvent was decanted. The residual orange material was extracted selectively with benzene and then the volume of benzene was reduced under vacuum until a slight crystallization was evident. The mixture was slowly cooled to 0°C and crystallization was completed by addition of ether. The product was filtered, washed with cold ether and dried in vacuo. The yield of the orange microcrystalline hydride was 32%.

9. Stock solution of anhydrous HBF_4 (83):

The stock solutions of anhydrous HBF_4 were prepared prior to its use by dropwise addition of 2 ml of aqueous 37% HBF_4 (~11 mmoles of HBF_4) into 10 ml of acetic anhydride which was stirred and maintained at 0°C with an ice-bath.

10. Protonation of the anion $Fe(CO)_3NO^-,Na^+$ 1 in THF in the presence of triphenylphosphine:

Formation of hydride 4 or cation 9:

0.7g of anion 1 $Fe(CO)_3NO^-,Na^+$ (3.1 mmole) and 2.00 g of $P(C_6H_5)_3$ (7.6 mmole, ~2.5 equivalents) were dissolved into 70 ml of THF cooled with an ice bath. On the stirred solution, 5 ml of th HBF_4 stock solution (1.5 eq. of HBF_4) were added dropwise. Stirring was discontinued after two hours, and the homogeneous solution brought to dryness under vacuum at room temperature. After washing the residue with 20 ml of ether, extraction with benzene followed by crystallisation in benzene/pentane yielded 0.66 g(30%) of 4 identified by IR and ^{1}H NMR (δ Fe-H = -4.9 ppm, JP-H = 79 ± 1 Hz in $CDCl_3$ at 37°C; we thank Dr. J.Y. Merour for this preparation). When different molar ratios of the reagents were used, the cation $(P(C_6H_5)_3)_2Fe(CO)_2(NO)^+BF_4^-$ 9 was formed instead (in variable yields depending upon the reaction conditions). Precipitation from the reaction mixture was either spontaneous or had to be induced by addition of diethyl ether, that could coprecipitate also some protonated phosphine $(C_6H_5)_3PH^+,BF_4^-$. In the procedure described below, a maximum yield of 50% was obtained. $Fe(CO)_3NO^-Na^+$ (0.37 g, 1.6 mmole) and $P(C_6H_5)_3$ (2.1 g, 8.0 mmole, 5 eq.) in 50 ml of THF were protonated as described above with 10 ml of the HBF_4 stock solution (∿ 5.5 eq.). IR of the solution after acidification indicated complete disappearance of 1 and the formation of an intermediate with CO's identical to that of hydride 3. Stirring was continued for an additional two hours (temperature of reaction mixture kept cold with ice bath) by that time a yellow precipitate had started to form. After stirring an additional six hours at room temperature the solid was filtered, washed with THF, dried and extracted with $CHCl_3$. Crystallization in $CHCl_3$/pentane yielded 0.6 g

(50%) of cation 9 $(P(C_6H_5)_3)_2Fe(CO)_2NO^+BF_4^-$ with IR spectra (KBr or $CHCl_3$) identical to that of an authentic sample prepared by reacting $(P(C_6H_5)_3)_2Fe(CO)_3$ with $NO^+BF_4^-$ in methylene chloride (181).

- Anal. Calcd. for $C_{38}H_{30}BF_4FeNO_3P_2$: C,60.5; H, 4.0; N, 1.9; P, 8.2. Found: C,60.4; H, 4.0; N, 1.9; P,8.2.

- IR (CH_2Cl_2); ν (CO) : 2050(s) cm^{-1}, 1990(vs)cm^{-1}
  ν (NO) : 1790(vs) cm^{-1}

- Reported (84) ; ν (CO) : 2050(s) cm^{-1}, 1993(vs) cm^{-1}
  ν (NO) : 1788(vs) cm^{-1}

11. $HFe(CO)_2(NO)(P(C_6H_5)_3)$ 3 synthesis in solution; oxidation, thermal decomposition:

Trifluoroacetic acid (0.13 ml, 0.2 g, 1.8 mmole) diluted with ether (5 ml) was added dropwise with a syringe to a stirred, ice cold solution of $Fe(CO)_3(NO)^-$, Na^+ 1 (0.33 g, 1.5 mmole) and triphenylphosphine (0.45g, 1.7 mmole) in 35 ml of ether. An IR spectrum recorded shortly after the addition (2 min) indicated the formation of hydride 3. The solution was cooled with a a dry ice-acetone bath and CF_3COO^-,Na^+ (solid) was decanted by gravity. The clear yellow-orange solution was used for ^1H and ^{31}P NMR. The solutions were extremely oxygen sensitive. An IR cell was filled under argon and the IR spectrum of 3 was recorded. The solution in the cell was transferred back into a syringe with no precautions to exclude air. The solution became dark immediately and the IR spectrum indicated total decomposition of 3 and formation of $(P(C_6H_5)_3)Fe(CO)_4$ 7, $(P(C_6H_5)_3)Fe(CO)(NO)_2$ 12 and small amounts of $(P(C_6H_5)_3)_2Fe(CO)_3$ 8 and $(P(C_6H_5)_3)_2Fe(NO)_2$ 6. In order to compare with anion 1, the same procedure was applied to a concentrated solution of anion 1 in ether. Only negligible modification of the IR spectrum and the formation of a small amount of $Fe(CO)_2(NO)_2$ 10 were observed.

The temperature of the solution of hydride 3 was brought to room temperature under argon. Hydride 3 decomposed into 6, 7, 8, and 12 within 4 hours. During the decomposition, some hydride 4 was precipitated from the solution which indicated that some free (uncomplexed) triphenylphosphine was released and reacted with undecomposed 3 to form 4. The degradation was much more rapid when solutions similarly prepared were concentrated under reduced pressure in order to attempt the isolation of the compound.

- IR (ether) ; ν (CO) : 2020(m) cm^{-1}, 1960(s) cm^{-1}
  ν (NO) : 1755(s) cm^{-1}

12. Reaction of hydride 3 with triphenylphosphine; conversion into hydride 4:

Trifluoroacetic acid (0.09 ml, 0.14 g, 1.2 mmole) was added dropwise to a stirred solution of $Fe(CO)_3(NO)^-$, Na^+ (0.25 g, 1.1 mmole) and $P(C_6H_5)_3$ (0.34 g, 1.3 mmole) in 27 ml of ether (cooled with a water-ice bath). After stirring two minutes, the reaction mixture was cooled with a dry ice-acetone bath. Solid $P(C_6H_5)_3$ (1.36 g, 5.2 mmoles or 5 equivalents) degased under vacuum was added to the stirred solution. The temperature was allowed to rise to ∿ 5°C and was maintained at this temperature with a water-ice bath. Precipitation of 4 with concurrent gas evolution occurred and no hydride 3 was present after 40 minutes (IR monitoring of the solution). The solution contained (IR, TLC) small amounts of 4, 6, 7 (traces) and 8 with no $[P(C_6H_5)_3]Fe(CO)(NO)_2$ 12 detected. The solid was filtered, washed with 20 ml of ether and extracted with benzene. Crystallization in benzene/pentane afforded 0.51 g of 4 (64%) identified by IR and ^1H NMR (δ Fe-H = -5.0 ppm, J(P-H)= 79 ± 1 Hz, in CH_2Cl_2 at 37°C).

13. Partial conversion of hydride 4 into hydride 3 under CO:

0.25g of 4 were dissolved in 10 ml of THF under argon. The orange solution darkened rapidly when CO was passed through the solution and afer 20 min no further change in the relative intensities of the ν CO's and ν NO's of 3 and 4 was observed. Again the stability of the solution under CO was dramatically affected by impurities. In one experiment where preliminary purging of the argon line was omitted, the presence of a contaminant (which could have been an olefin) caused rapid formation of the degradation products 6, 7, 8, 12. No evidence for the formation of 3 was obtained in that case. We have indeed observed very recently the rapid decomposition of 3 in the presence of dienes (4 was left unchanged) at 25°C.

14. HFe(CO)(NO)(dppe):

To a stirred ice cold THF (100 ml) solution of anion $Fe(CO)_3NO^-,Na^+$ 1 (1g, 4.5 mmole) and 1.2 equivalent of dppe (2g, 5.0 mmoles) was slowly added (10 min.) 1.5 equivalent of anhydrous (stock) HBF_4 (7.4ml, 6.5 mmoles). After stirring one hour at 0°C and ½ hour at room temperature, the homogeneous solution was subjected to vacuum until complete evaporation of the THF. The yellow residue was washed with ether and extracted with benzene. Crystallization in benzene/CH_3CN afforded HFe(CO)(NO)(dppe) in 65% yield (we thank Dr. J.Y. Merour for this preparation).

Note: dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$

- IR(CH_2Cl_2); ν(CO) : 1940(s) cm^{-1}
  ν(NO) : 1710(s) cm^{-1}

- ^1H NMR: TMS internal reference, solvent $CDCl_3$,
  δH aromatic : multiplet between 7.86 and 6.82 ppm;
  $\delta(CH_2)$: 2.04 ppm, doublet J(P-H) = 18Hz,
  δH-Fe : -3.35 ppm, triplet J(P-H)= 25 Hz.

15. Protonation of anion 1 $Fe(CO)_3NO^-,Na^+$ in the absence of triphenylphosphine in hexane, hexane-water or ether

0.15 g of anion 1 (0.67 mmole) was suspended in 10 ml of hexane and the stirred suspension cooled with a water-ice bath. 0.04 ml of CF_3COOH (0.54 mmole, 0.8 equivalent) was added rapidly. The hexane solution became immediately colored. The IR spectrum was composed of the absorptions characteristic of $Fe(CO)_2(NO)_2$ (one of the reported decomposition product of $HFe(CO)_3NO$ (74); ν CO = 2090 s, 2040 s, ν NO = 1810 s, 1770 vs (in cm^{-1}) (178)) and two other absorptions at 2020 and 2000 cm^{-1} indicating that at least another compound X was present in this solution. Both products were volatile and could be transferred with the solvent into a trap at -196°C by distillation at room temperature under vacuum. Apart from unreacted 1 no other nitrosyl complex could be detected in the solid residue left behind which was redesolved in THF. After warming to room temperature, the orange hexane solution was reacted with an excess of triphenylphosphine (1,41 g, 5.4 mmole, 8 equiv.) which dissolved partially. After two hours of stirring $Fe(CO)_2(NO)_2$ was totally transformed into the non volatile monosubstitution product $Fe(CO)(NO)_2(P(C_6H_5)_3$ (ν CO= 2010 s, ν NO = 1765 s, 1725 vs cm^{-1}) and a trace of $Fe(CO)_2(P(C_6H_5)_3)_2$ (T.L.C.). X which did not react was transferred again into a cooled trap. At room temperature the very pale yellow solution exhibited only the two ν CO observed previously at 2020 and 2000 cm-1. The nature of this material is unknown at present. However, based on the thermal stability, the lack of reaction with $P(C_6H_5)_3$ and the ν CO values, it cannot be $H_2Fe(CO)_4$(182), the other reported (74) decomposition product of the hydride $HFe(CO)_3NO$.

The same results were obtained when the protonation with CF_3COOH was run in ether. Conversion into $(P(C_6H_5)_3)Fe(CO)(NO)_2$ was however faster (less than 1 hour) and formation of a trace amount of $(P(C_6H_5)_3)_2=Fe(CO)_3$ (T.L.C.) was also detected.

The same mixture of volatile products also resulted from the protonation with aqueous 37% HBF_4. In that case, 1 was dissolved in distilled water and hexane added. After acidification and rapid stirring, the organic phase became rapidly colored with an IR spectrum identical to those described above.

16. Preparation of $[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ 32:

HBF_4/acetic anhydride (1.2 ml (stock), 1.8 mmoles) was added dropwise over a period of 5 minutes to a stirred ice cold THF: ether (1:1) (40 ml total) solution of $H\text{-}Fe(CO)(NO)(P(C_6H_5)_3)_2(C_6H_6)$ 4 (1 g, 1.4 mmole). Precipitation of an ocre solid started immediately. Once the addition completed, the ice bath was removed and stirring was continued at room temperature until H_2 evolution ceased (approx. 10 minutes). Once the reaction was completed, the mixture was then cooled to 0°C to complete the precipitation. The orange-brown powder was collected, washed with ether and dried in vacuo (0.87g, 86% yield).

The same procedure was applied for the preparation in "pure" THF and in "pure" ether (84% yield).

The organge-brown complex is unstable in solvents such as methylene chloride, chloroform, acetone, etc. and undergo a slow decomposition (several days) under argon in the solid state.

17. Solid-gas reaction of $[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ 32 with carbon monoxide:

A small portion of $[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$(1g) was placed in a schlenk under approximately one atmosphere of carbon monoxide at room temperature. The colour of the powder gradually changed from ocre to yellow. The reaction was completed after 3 days.

A KBr pellet was pressed and the IR spectrum of the metal-CO and metal-NO was recorded. This spectrum consisted of three peaks at 2040 cm^{-1}, 2000 cm^{-1} and 1790 cm^{-1}. IR in acetonitrile consisted of three peaks at 2060 cm^{-1}, 2010 cm^{-1} and 1800 cm^{-1}. This pattern indicated the formation of the cation $[Fe(CO)_2(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ with absence of any other compounds containing CO and/or NO ligands. IR spectra (crystallization in CH_2Cl_2/hexane) were also identical to those of samples prepared directly from the reaction of $Fe(CO)_3(P(C_6H_5)_3)_2$ with $NO^+BF_4^-$ (181) or from the protonation of $Fe(CO)_3NO^-,Na^+$ 1 in THF in the presence of triphenylphosphine.

18. Solid State Reaction of $[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ 32 and $[Fe(CO)(NO)(P(C_6H_5)_3)_2(CH_3CN)]^+BF_4^-$ 33 with KBr

A small portion of 32 or 33 and approximately ten times as much KBr were placed in a vial mortar and the mixture was crushed and mixed with a pestle. A pellet was pressed and the IR spectrum of the metal-CO and metal-NO region was recorded. This spectrum consisted of two peaks of equal intensity and width at 1920 cm^{-1} and 1695 cm^{-1}. This pattern matched those previously reported (136). This was verified by allowing 33 to react with $[C_6H_5CH_2N(CH_3CH_2)]^+,Br^-$ in acetonitrile to form $BrFe(CO)(NO)(P(C_6H_5)_3)_2$ and comparing the infrared spectra. Both were identical.

19. Preparation of $[Fe(CO)(NO)(P(C_6H_5)_3)_2(CH_3CN)]^+BF_4^-$ 33:

$[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4$ 32 was dissolved in a minimum amount of acetonitrile. The solution was gradually cooled to 0°C and ether was slowly added to complete the crystallization. These brown crystals were filtered out, washed with pentane and dried in vacuo (80% yield starting from hydride 4).

The crystalline compound 33 is soluble without decomposition in solvents such as methylene chloride, chloroform, acetone and is air-stable in the solid state for several months.

- Anal. Calcd. for $C_{37}H_{30}FeNO_2P_2BF_4$ (1.5 CH_3CN) C, 61.1 ; H, 4.4 ; N, 4.4 . Found : C, 60.3 ; H, 4.5; N, 4.1.

- IR(CH_3CN); ν (CO): 1960(s) cm^{-1}
  ν (NO): 1750(s) cm^{-1}

- ^1H NMR : TMS internal reference, solvent $CDCl_3$, δ C_6H_5: 7.58 ppm, δ CH_3CN solvate : 2.05 ppm, large singlet, δCH_3CN ligand : 1.58, triplet J(P-H) ≈ 2 Hz.

20. Preparation of $ClFe(CO)(NO)(P(C_6H_5)_3)_2$ $(34)_1$, from 32:

$BF_4Fe(CO)(NO)(P(C_6H_5)_3)_2$ (0.40g, 56 mmole) was added portionwise to a solution of $(P(C_6H_5)_3)_2N^+,Cl^-$ (0.96g, 1.7 mmole) in acetonitrile (6 ml) at room temperature. The corresponding neutral five coordinate complex precipitated spontaneously as a brown crystalline solid. The reaction mixture was left to stand for 5 minutes, then cooled to 0°C to complete crystallization. These relatively air-stable crystals were filtered, washed with cold acetonitrile, and dried in vacuo (83% yield). The infrared spectrum matched those previously reported (136).

IR (CH_2Cl_2) ; ν(CO) : 1925(s) cm^{-1}
ν(NO) : 1700(s) cm^{-1}

21. Preparation of $BrFe(CO)(NO)(P(C_6H_5)_3)_2$ (<u>34</u>)2 from <u>32</u>:

$BF_4Fe(CO)(NO)(P(C_6H_5)_3)_2$ (0.20g; 0.28 mmole) was added portionwise to a solution of $C_7H_7N(CH_3CH_2)_3^+,Br^-$ (0.22g ; 0.83 mmole) in acetonitrile (6 ml) at room temperature. The corresponding neutral five coordinate complex precipitated spontaneously as a brown crystalline solid. The reaction mixture was left to stand for 5 minutes then cooled to 0°C to complete crystallization. These relatively air-stable crystals were filtered, washed with cold acetonitrile, and dried in vacuo (69% yield). The infrared spectrum matched those previously reported (136).

$IR(CH_2Cl_2)$; ν (CO) : 1930(s) cm^{-1}
ν (NO) : 1710(s) cm^{-1}

22. Preparation of $IFe(CO)(NO)(P(C_6H_5)_3)_2$ (34)3 from 32:

$BF_4Fe(CO)(NO)(P)C_6H_5)_3)_2$ (0.20g ; 0.27 mmole) was added portionwise to a solution of anhydrous sodium iodide (0.13g 0.81 mmole) in acetonitrile (4 ml) and anhydrous ether (2 ml) at 20°C. The corresponding neutral five coordinate complex precipitated spontaneously as a brown crystalline solid. The reaction mixture was left to stand for 5 minutes then cooled to 0°C to complete crystallization. These relatively air-stable crystals were filtered, washed with cold acetonitrile, and dried in vacuo (57% yield). The infrared spectrum matched those previously reported (136).

IR(CH_2Cl_2) ; ν(CO) : 1930(s) cm^{-1}
ν(NO) : 1710(s) cm^{-1}

Anal. Calcd. for $C_{37}H_{30}FeINO_2P_2$: C, 58.1%
H, 3.9% ; N, 1.8%; P, 8.1%. Found: C, 58.9%;
H, 4.1%; N, 1.6%; P, 7.9%

23. Reaction of $XFe(CO)(NO)(P(C_6H_5)_3)_2$(X=Cl, Br and I) with $AgPF_6$:

$AgPF_6$ (20 mg, 0.093 mmole) was dissolved in acetone (2 ml) (dry over B_2O_3) and 10 drops of CH_3CN was added. $ClFe(CO)(NO)(P(C_6H_5)_3)_2$ (40 mg, 0.055 mmole) was added portionwise. A brown product precipitated. The solid was filtered and dried under vacuo. The IR spectrum of the solid in CH_3CN showed bands at 1965 cm^{-1} (ν CO) and 1750 cm^{-1} (ν NO) characteristic of $[Fe(CO)(NO)=(P(C_6H_5)_3)_2(CH_3CN)]^+ PF_6^-$. The same procedure was followed for X=Br and I and the same results were obtained.

24. Preparation of $N_3Fe(CO)(NO)(P(C_6H_5)_3)_2$ (<u>34</u>)4:

$BF_4Fe(CO)(NO)(P(C_6H_5)_3)_2$ (0.050g, 0.069 mmole) was added portionwise to $(P(C_6H_5)_3)_2N^+,N_3^-$ salt (0.60g; 0.10 mmole) dissolved in acetonitrile (5ml). The neutral azide complex precipitated spontaneously as a light brown crystalline solid. The reaction mixture was left to stand for 3 minutes then cooled to complete crystallization. These relatively air-stable crystals were filtered, washed with cold acetonitrile and dried in vacuo (43% yield). The infrared spectrum matched that previously reported (136, 138).

IR(CH_2Cl_2) ; ν (CO) : 1925(s) cm^{-1}
ν (NO) : 1670(s) cm^{-1}
ν (N_3) : 2060(s) cm^{-1}

25. Protonation of 4 with anhydrous HBF_4 in the presence of excess triphenylphosphine and carbon monoxide to give 9

Anhydrous HBF_4 (0.35 ml, 0.32 mmole) was added dropwise, at room temperature, to a stirred solution of hydride 4 (0.11g, 0.16 mmole) and triphenylphosphine (0.42g, 1.6 mmole) in THF (10 ml), saturated with carbon monoxide (carbon monoxide was passed through the solution during addition). Cation 9 precipitated gradually as a mixture with sodium trifluoroborate. After stirring for thirty minutes, the reaction mixture was cooled to 0°C and the solid was filtered. The yellow-white powder was washed with ether and subsequently extracted selectively with chloroform. Afterwards, the volume of the solution was reduced under vacuum until a slight crystallization appeared. The mixture was cooled to 0°C and the crystallization was completed by adding ether. These crystals were collected, washed with cold ether and dried in vacuo. The orange cation 9 was obtained in 55% yield.

26. Reduction of cation 9 with $(CH_3CH_2)_3BH^-,Li^+$ to form anion 57:

A suspension of cation 9 in THF (0.05g. 0.066 mmole) was frozen at -196°C under argon. After addition of the required amount of $(CH_3CH_2)_3BH^-,Li^+$ (1M solution in THF, $\approx$ 6 equivalents), the temperature was allowed to raise. As soon as melting occurred, stirring was started. Gas evolution began around -20°C and became vigorous at approximately 0°C as the solid gradually solubilized. The solutions of anion 57 were yellow in colour and those containing the degradation products were greenish.

IR(THF) ; ν(CO) : 1920(s) cm^{-1}, 1850(s) cm^{-1}
1895(w) cm^{-1}, 1820(w) cm^{-1}

ν(NO) : 1550(s) cm^{-1}
1600(s) cm^{-1}

For gas phase analysis, the cooled reaction flask was rapidly connected to a vacuum line. Upon warming to 20°C, evolved gases could be isolated in different bulbs for subsequent mass spectometric analysis, or the gases were directly passed through a previously calibrated V.P.C. apparatus which was capable of separating H_2, CO_2, O_2, N_2 and CH_4 (molecular sieve column).

In the low temperatures NMR experiments, a CH_2Cl_2 + THF solution of cation <u>9</u> in the NMR tube was cooled to -78°C and the appropriate amount of reducing agent $(CH_3CH_2)_3BH^-,Li^+$ was added. Argon was slowly passed through the solution to ensure adequate mixing. The tube was quickly transferred into the probe of the spectrometer, after securing the tube with a cap tight enough to withstand the pressure developing as the reaction proceeded.

27. Reduction of hydride <u>4</u> with $(CH_3CH_2)_3BH^-,Li^+$ to form anion <u>58</u> and its reaction with carbon monoxide:

The reduction could be performed in a flask or directly in the NMR tube as follows. The reduction was done directly in the ^{31}P NMR tube by dissolving hydride <u>4</u> (0.05g, 0.07 mmole) in 4.5 ml of THF. To the stirred solution was added 0.4 ml of a 1M THF solution of $(CH_3CH_2)_3BH^-,Li^+$ (6 equivalents). After stirring one hour at room temperature, the ^{31}P NMR of the red solution was taken. A single peak at $\delta = +81.4$ in the ^{31}P NMR spectrum indicated complete conversion of hydride <u>4</u> into the anion <u>58</u>.

The red solution gradually turned yellow on passing carbon monoxide through the solution during 10 minutes, indicating transformation of anion <u>58</u> into anion <u>57</u>.

As expected, on the basis of an overall 100% conversion of hydride <u>4</u> into anion <u>5</u>, the ^{31}P NMR spectrum of the solution showed only two peaks. One peak corresponding to uncoordinated triphenylphosphine ($\delta = 5.17$ ppm) and the other corresponding to $(P(C_6H_5)_3)=Fe(CO)_2(NO)^-,Li^+$ <u>57</u> ($\delta = +78.3$ ppm), in a ratio of 1:1.

When using a limited amount of reducing agent (1.1 equivalent) for the conversion of hydride <u>4</u> into anion <u>58</u>, it was necessary to heat at 50°C during 2 hours to achieve total conversion.

The yield of anion <u>57</u> from the reduction of cation <u>9</u> was obtained by comparing the intensity of the ν CO at 1920 cm^{-1} to that of solutions of <u>57</u> of known concentrations resulting from the reduction of hydride <u>4</u>. A

Perkin-Elmer 283 apparatus operating in the absorbance mode was used for this purpose.

28. Reduction of Hydride 4 Using Na/Hg Amalgam:

Hydride 4 (0.40g, 0.62 mmole) was added portionwise to a stirred 100% excess sodium amalgam (6.2 mmole Na, 4 ml Hg) in 20 ml of THF. The reaction mixture was stirred, at room temperature, for 2½ hours. Upon filtration of the reaction mixture (taking extreme precautions of excluding air), a dark red solution of the sodium salt of anion 58 was obtained.

IR(THF) ; ν(CO) : 1830(s) cm^{-1}, 1780(w) cm^{-1}
ν(NO) : 1540(s) cm^{-1} - cm^{-1}

29. Formyl Complex 56 (^{31}P NMR and ^{1}H NMR)

For the ^{31}P NMR, the reaction was done directly in the tube by dissolving cation 9 (0.05g) in 5 ml of CH_2Cl_2. The temperature of the solution was lowered to -78°C and 1.5 equivalent of $(CH_3CH_2)_3BH^-Li^+$ was added.

The temperature was maintained around -70°C until transferred into the probe of the spectrometer. The ^{31}P NMR showed the formation of the formyl $(P(C_6H_5)_3)_2(NO)(CO)Fe-CHO$ 56 (δ = +64.3 ± 0.2 ppm at 50°C) with some cation 9 remaining (the ratio of 56/9 was approximately 3). Decomposition started to appear around -40°C followed by fast decomposition at about -30°C.

The samples for ^1H NMR were prepared similarly. The ^1H NMR showed conclusively the formation of the formyl 56 with δ = 13.5 ppm and (triplet) J(P-H)=10 Hz.

30. $Fe(CO)(NO)(C_3H_5)(P(C_6H_5)_3)$ 60 prepared from hydride 4:

To a stirred solution of 4 (0.5g, 0.78 mmole) in 5 ml of THF was added 1.3 equivalent of $(CH_3CH_2)_3BH^-,Li^+$. After stirring at least 2 hours at 50°C, the temperature of the dark red solution was brought to room temperature.

Allyl bromide (1.3 equivalents) was added to the anion and the solution was stirred for 5 minutes. After evaporation under reduced pressure the product was chromatographed on alumina prepared in hexane.

Hexane:benzene (1:1) eluted $Fe(CO)(NO)(C_3H_5)(P(C_6H_5)_3)$ 60 in 63% yield (176).

Note: The alumina used for chromatography is a product from Merck (Al_2O_3 90, activity II-III, neutral, 70-230 mesh A.S.T.M.).

31. $(P(C_6H_5)_3)Fe(CO)_2NO^-$ 57 prepared from hydride 3 and its reaction with allyl bromide:

Trifluoroacetic acid (0.38 ml, 0.57g, 4.9 mmole) was added dropwise to a stirred solution of $Fe(CO)_3NO^-,Na^+$ 1 (1.0g, 4.4 mmole) and triphenylphosphine (1.35g, 5.2 mmole) in 100 ml of ether at 0°C (water-ice bath). After the addition was completed, the reaction mixture was stirred for 2 minutes and 1.5 equivalents of $(CH_3CH_2)_3BH^-,Li^+$ (7.7 ml of a 1M THF solution) was added. Gas evolution occurred and the solution became slightly red. After stirring for one minute, IR of the solution indicated formation of the anion 57.

Addition of 1.3 equivalents of allyl bromide to the above solution of anion 57 or to a solution of anion 57 prepared directly from cation 9 or by Na/Hg amalgam reduction of 14 afforded a 3:5 (based on IR absorptions intensities) mixture of allyl $(C_3H_5)Fe(CO)(NO)(P(C_6H_5)_3)$ 60 and $(C_3H_5)Fe(CO)_2(NO)$ 62, after stirring for 15 hours. An intermediate (probably the σ allyl) was formed as soon as the allyl bromide was added. It evolved gradually into 60 and 62.

32. Preparation of $CH_3COC_3H_4Fe(CO)_2NO$ (184):

Some acyl derivatives of cobalt are recognized as important intermediates in hydroformylation and related carbonylation reactions (90). It was worthwhile to study analogous systems since anion 1 was readily available. The following preparation was modelled on those of Otsuka and Nakamura (183).

$Fe(CO)_3NO^-,Na^+$ (3.9g, 2×10^{-2} moles) was dissolved in 200 ml of THF and 1.35 liter of gaseous allene was introduced into the yellowish brown solution at 0°C.

3.7 ml of CH_3I was added dropwise at 0°C and the reaction mixture was slowly warmed up to room temperature and stirring was maintained overnight. IR of the solution indicated the absence of any metalates. After filtration and evaporation under reduced pressure the product was chromatographed on aluminum (Merck: Al_2O_3 90, activity II-III, neutral, 70-230 mesh A.S.T.M.) prepared in hexane and eluted with benzene. Upon evaporation of the solvent, a dark red oil was obtained in 30% yield (184).

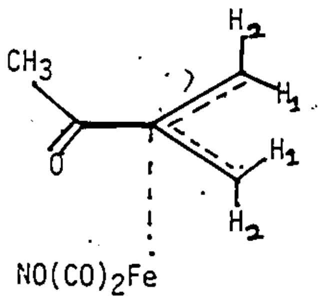
Mass spectroscopy indicated $(m/e)^+ = 225$ and peaks corresponding to successive loss of two CO and NO.

IR(THF); ν (C=O): 2050(s) cm^{-1}, 2000(s) cm^{-1}

ν (C=O): 1685(w) cm^{-1}

ν (NO) : 1775(s) cm^{-1}

H NMR : TMS internal reference, solvent CD_2Cl_2 (37°C)
or CD_3COCD_3 (-60°C)



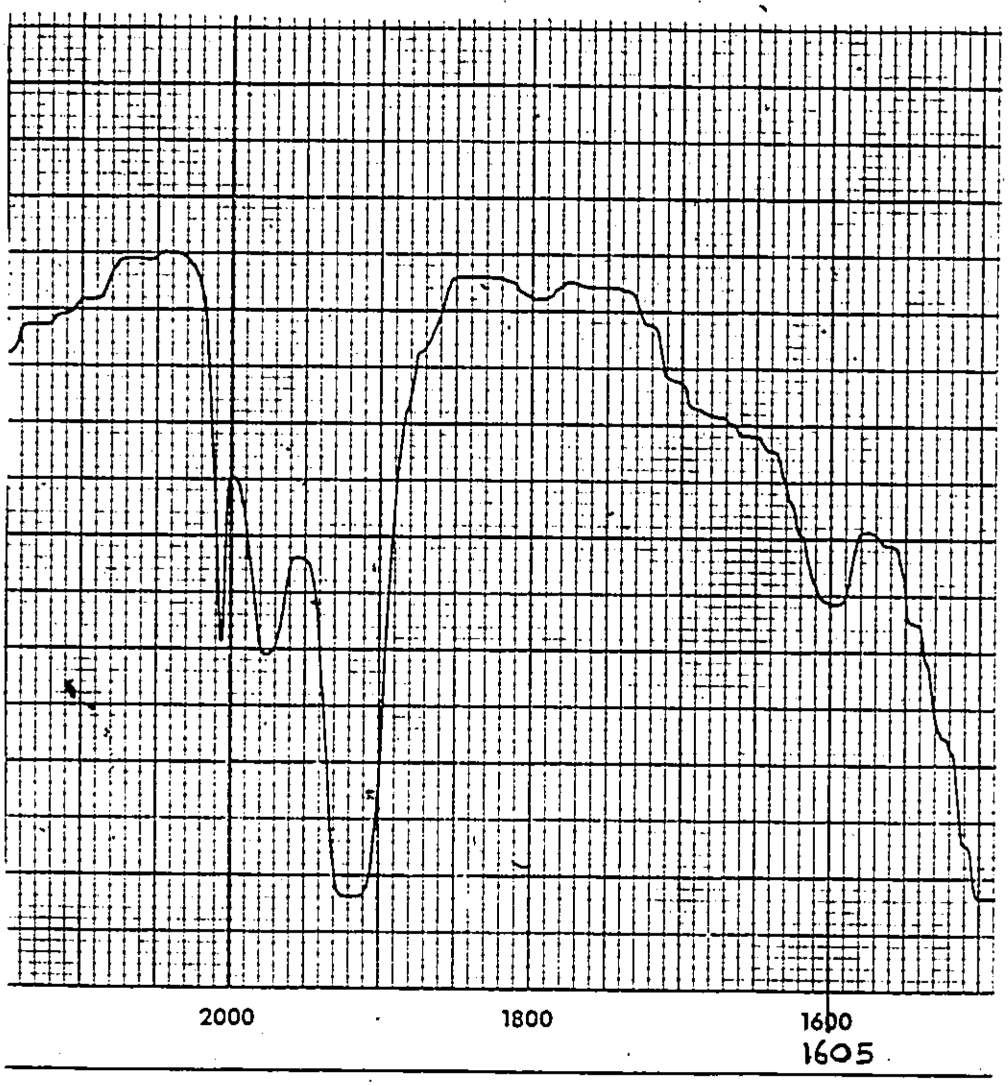
$\delta(H_1)$ = 3.55 ppm, singlet

$\delta(H_2)$ = 4.67 ppm, singlet

$\delta(CH_3)$= 2.17 ppm, singlet

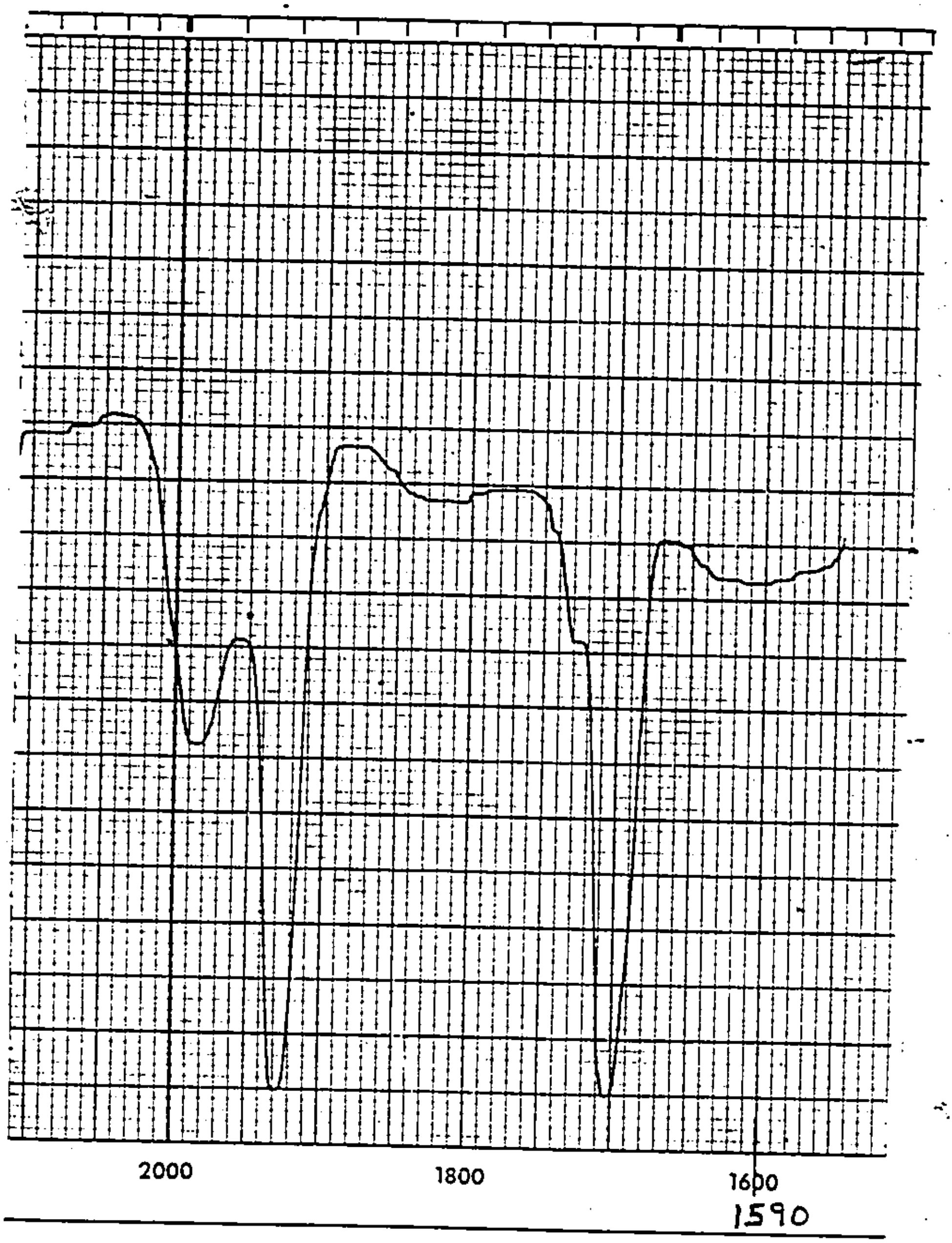
Infrared Spectrum of Selected Complexes
In The ν CO and ν NO Region
(Recorded on Unicam SP 1100)

1- $Fe(CO)_3NO^-$, Na^+ in ether

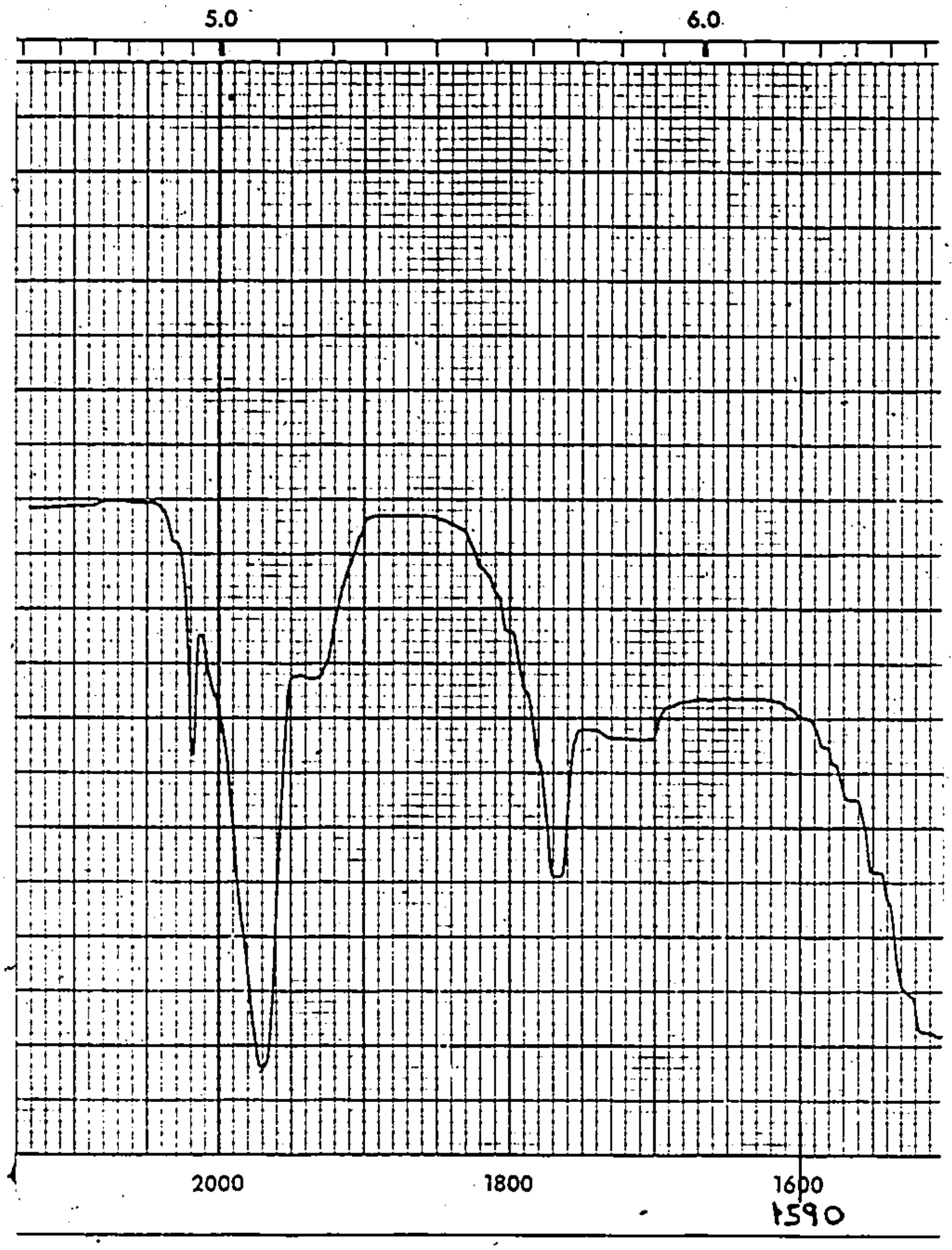


2- $Fe(CO)_3NO^-$, Na^+ in THF

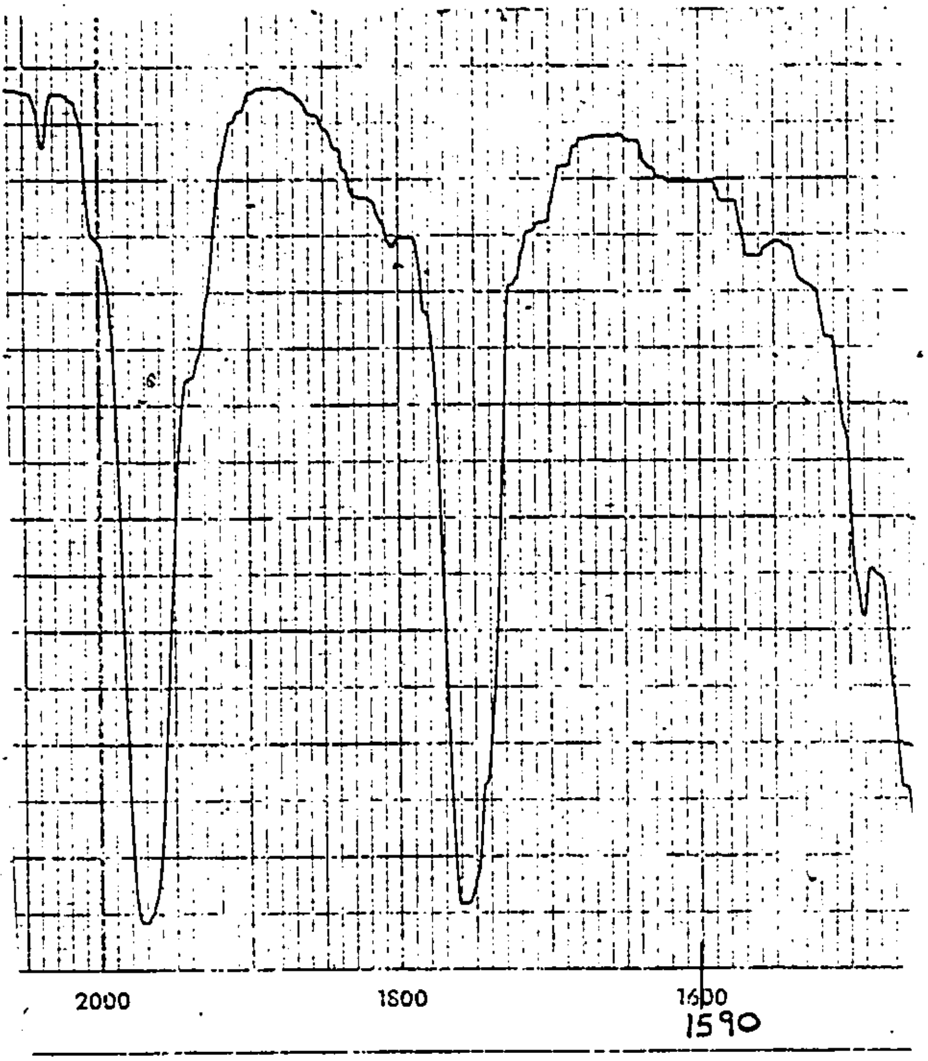
3- H-Fe(CO)(NO)$(P(C_6H_5)_3)_2$ in THF



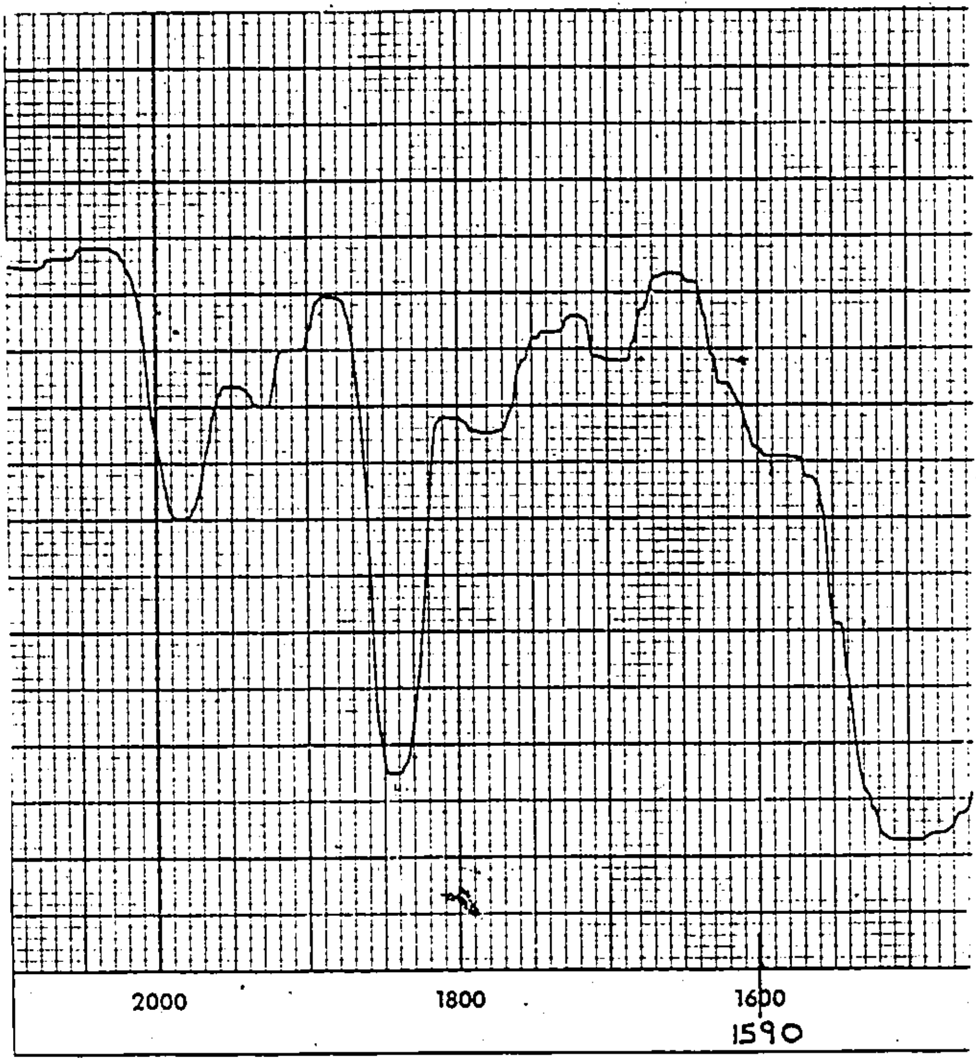
4- H-Fe(CO)$_2$NO(P(C$_6$H$_5$)$_3$) in ether



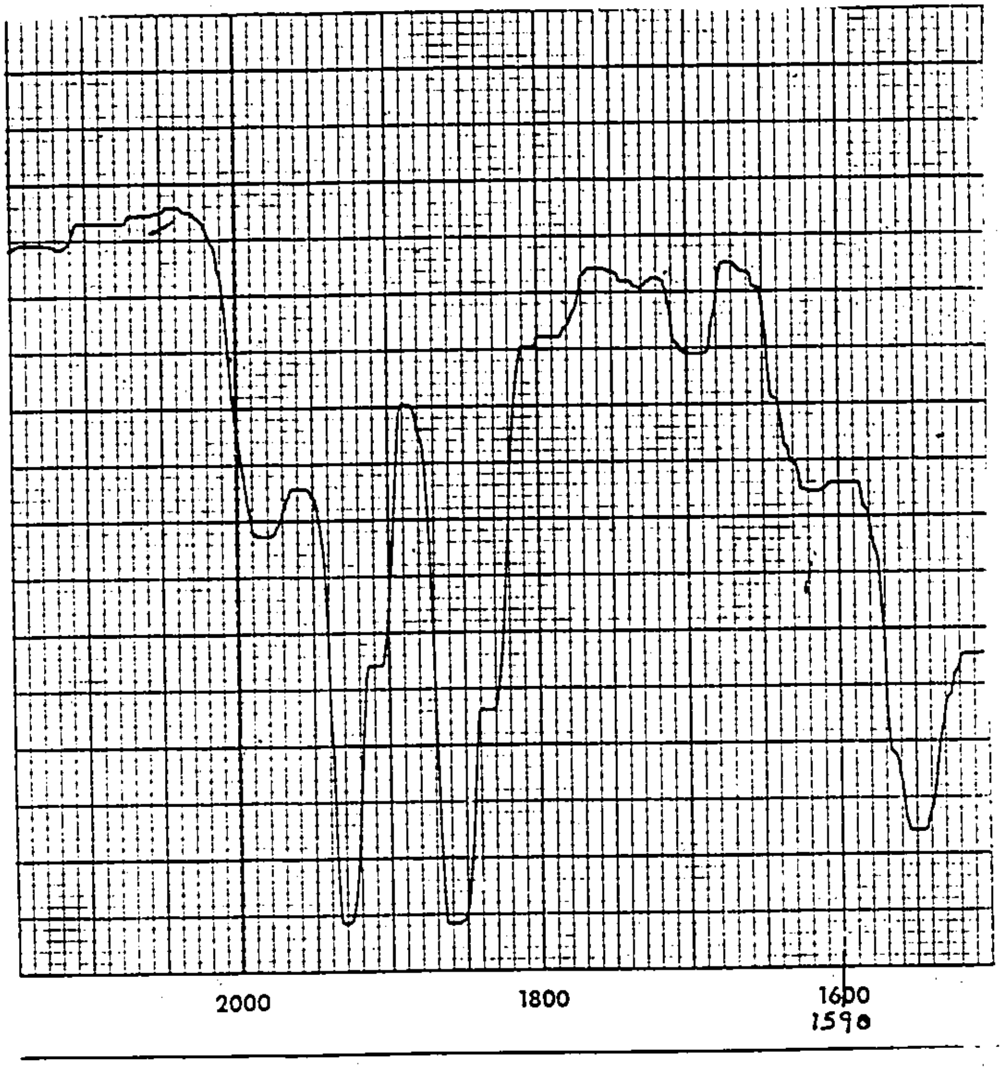
5- $[Fe(CO)(NO)(P(C_6H_5)_3)_2(CH_3CN)]^+BF_4^-$ in CH_2Cl_2



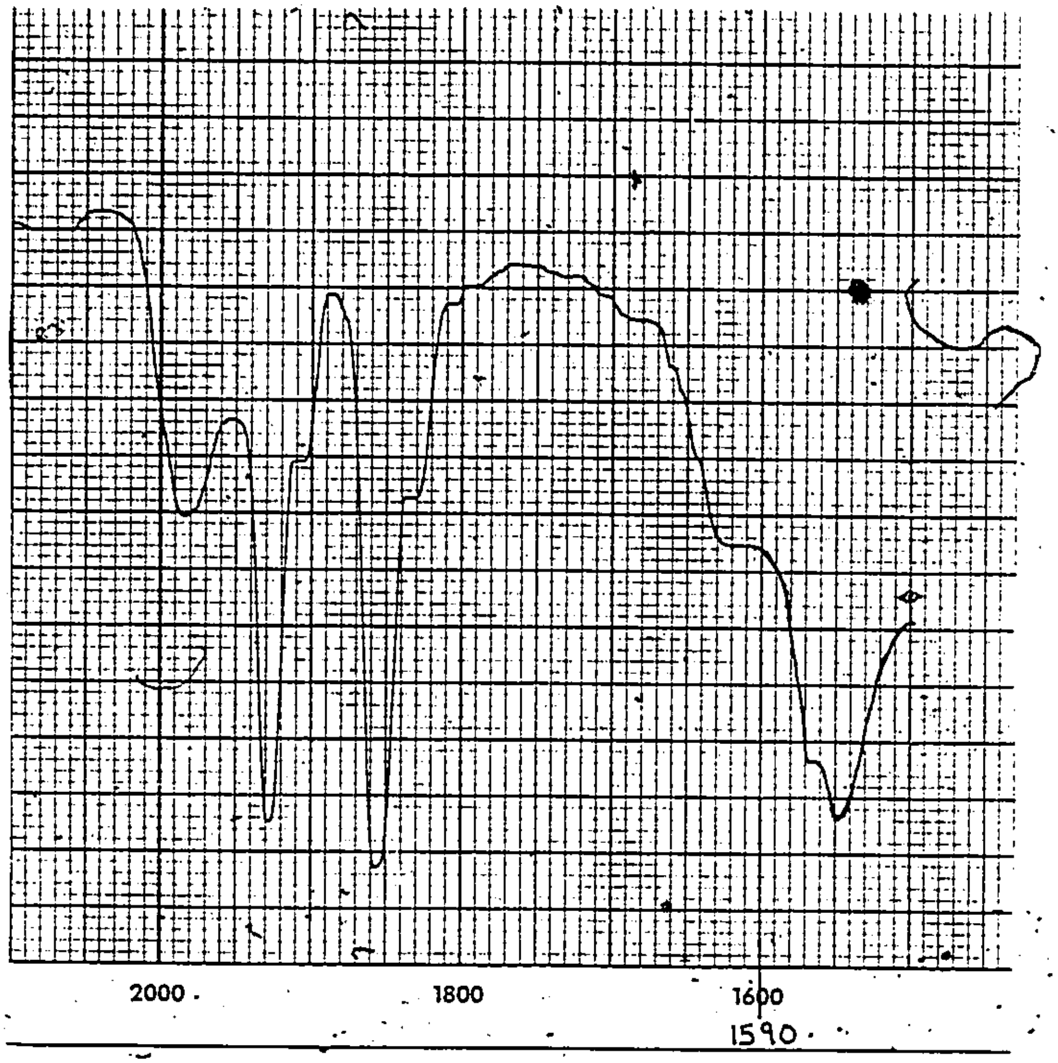
6- $(P(C_6H_5)_3)_2\,Fe(CO)(NO)^-, Li^+$ in THF prepared from hydride 4 and reducing agent 55



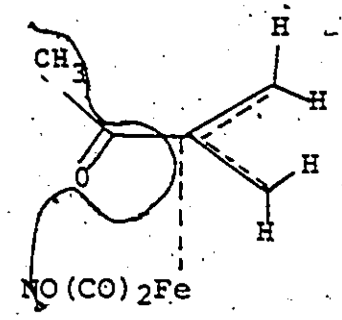
7- $(P(C_6H_5)_3)Fe(CO)_2(NO)^-, Li^+$ in THF by passing CO through anion <u>58</u>

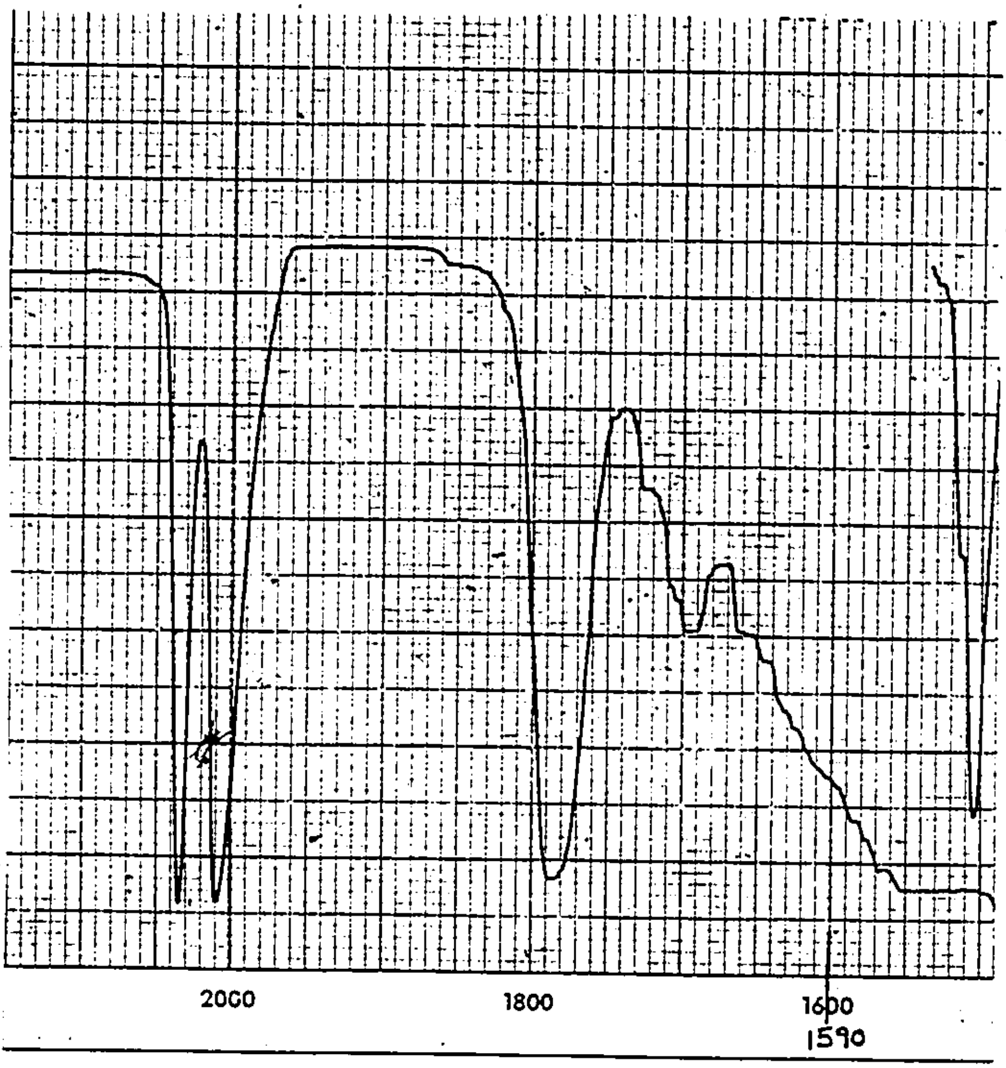


8- $(P(C_6H_5)_3)Fe(CO)_2(NO)^-,Li^+$ in THF prepared from cation 9 and reducing agent 55



9- $CH_3COC_3H_4Fe(CO)_2NO$ in THF





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CLAIMS TO ORIGINAL RESEARCH

1) Synthesis of two new hydrides:
   a) $HFe(CO)(NO)(P(C_6H_5)_3)_2$
   b) $HFe(CO)_2(NO)(P(C_6H_5)_3)$

2) The reactivity of iron nitrosyl hydrides towards substitution; it was shown that the NO ligand induces a greater accessibility to the coordination sphere of the metal.

3) Recognition for the first time of the solvent dependency on the protonation of the anion $Fe(CO)_3NO^-,Na^+$.

4) A new route to the cation $[Fe(CO)_2NO(P(C_6H_5)_3)_2]^+BF_4^-$ was developed.

5) First recognition of the instability of iron nitrosyl dimers with respect to ligand redistribution and fragmentation into new monometallic compounds.

6) Synthesis of the new highly reactive "pseudo coordinatively" unsaturated complex $[Fe(CO)(NO)(P(C_6H_5)_3)_2]^+BF_4^-$.

7) Synthesis of the new acetonitrile complex $[Fe(CO)(NO)(P(C_6H_5)_3)_2(CH_3CN)]^+BF_4^-$.

8) Demonstration of the high lability of the acetonitrile ligands in methatesis reactions.

9) First study of the reduction of the iron nitrosyl cation $[Fe(CO)_2(NO)(P(C_6H_5)_3)_2]^+BF_4^-$ with H^-.

10) Synthesis of the new anions $(P(C_6H_5)_3)Fe(CO)_2(NO)^-$, and $P(C_6H_5)_3)_2Fe(CO)(NO)^-$ in solution.

11) Characterization in solution of the formyl complex $(P(C_6H_5)_3)_2(NO)(CO)Fe-CHO$.

12) First investigation of the ion pairing phenomena observed for the iron carbonyl nitrosyl anions $Fe(CO)_x(NO)(L)_y^-$ $(x+y=3)$ in solutions.

13) Synthesis of the new acyl derivative $CH_3COC_3H_4Fe(CO)_2NO$.