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COMPLEXES OF ARYLDIAZENE AND ARYLHYDRAZIDE: PRODUCTS OF THE REACTIONS OF BENZENEDIAZONIUM IONS WITH TRANSITION METAL HYDRIDES

by

JAMES ALLEN CARROLL

A.B., Wabash College, 1965
M.S., California State University at San Jose, 1974

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
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ABSTRACT

Benzenediazonium salts with BF_4^- and PF_6^- counterions, or their 4-substituted derivatives, reacted with Cp_2WH_2 (Cp = η^5-C_5H_5) in toluene/methanol below 253 K to produce yellow 1:1 adduct salts in high yield. Proton magnetic resonance, with $^{15}N(1)$ substitution, allowed a nearly complete structural assignment of the cationic complex as $[Cp_2WH(N{=}NHAr)]^+$, a doubly-bent diazenido complex protonated at N(2) rather than N(1) as in all previous examples. This hydrazido(2-) ligand is believed to lie at 90° to the Cp_2WH midplane. In solution above 253 K the yellow salts underwent a novel rearrangement to a brown hydrazide complex $[Cp_2W\text{-}NH_2\text{-}NAr]^+$.

The low-temperature reaction of diazonium salts with Cp_2ReH produced a brown 1:1 adduct, difficult to purify, which was believed to be the expected diazene complex, $[Cp_2ReNH{=}NAr]^+$. It reacted with base to form the neutral diazenido complex. Similarly, from Cp_2MoH_2 the hydrazide $[Cp_2Mo\text{-}NH_2NAr]BF_4$ was identified in product mixtures, but this decomposed before it was isolated. With two moles of diazonium salt a distinct 1:2 adduct crystallized from the reaction mixture. On the basis of neutralization by triethylamine, this was identified as a bisdiazene complex $[Cp_2Mo(NHNAr)_2](BF_4)_2$.

With diazonium salts the monohydrides $IrH(CO)(PPh_3)_3$ and $IrH(CO)_2(PPh_3)_2$ also produced hydrazido(1-) complexes, identified by X-ray crystallography and spectroscopy as orthometalated. Geometry at the iridium is approximately square-based pyramidal with a triphenylphosphine on the axis. The four atoms of the aryldiazo chelate are coplanar; the iridium lies 9.4 pm out of this plane toward the apex. Bond lengths in the metallocycle indicate that the N-N bond order (N-N = 138.8(13) pm) is reduced at the expense of other bonds, compared to aryldiazenes. The hydrogens are located on each nitrogen and both are weakly bonded to the BF_4^- counterion. Reaction of $[Ir(NHNHC_6H_3G)(CO)(PPh_3)_2]BF_4$ (G=general substituent) with base produced the corresponding orthometalated iridium(I) diazenes. The hydrazido complexes were readily oxidized by dihalogens or air, producing previously known iridium(III) diazenes $[Ir(NHNC_6H_3G)(CO)(PPh_3)_2X]BF_4$ where X is the halide or, from air oxidation, F or FBF_3.

The reactions of benzenediazonium salts with transition metal complexes other than hydrides were not successful. With $Na[Fe\{S_2C_2(CN)_2\}_2]$ the diazonium salt attacked at the sulfur and the product of ligand abstraction and dinitrogen extrusion was isolated, ArSC(CN)C(CN)SAr. Experiments with $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Fe_2(CO)_6(SMe)_2$, $Na_2Fe(CN)_5NO$, $NaIrCl_5NO$, and $[Ru(NH_3)_5(OH_2)]Cl_2$ are also noted.

To Anne

Acknowledgements

During my rather lengthy residence in the Simon Fraser chemistry department the vast majority of its other members have been helpful, supportive, and/or encouraging to me. To start a list of individuals who have been particularly helpful would mean that the list would have to end with someone, and I feel it unfair to those who would be excluded. I have tried to express my appreciation all along and so will just take this opportunity to emphasize the sincerity of earlier acknowledgments.

I would like to thank the National Research Council of Canada for a Postgraduate Scholarship, which served as encouragement as well as financial support.

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List of Abbreviations and Symbols

A = general anion

Ac = acetyl, ethanoyl, CH_3CO-

Ar = aryl = substituted phenyl or phenyl

bipy = 2,2'-bipyridyl, $(C_5H_4N)_2$

Cp = η^5-cyclopentadienyl

dmso = dimethylsulfoxide

dppe = 1,2-bis(diphenylphosphino)ethane

Et = ethyl, C_2H_5-

G = general radical group: H, alkyl, aryl, silyl, acyl, aroyl, alkoxy, nitro, etc.

L = 2-electron donor ligand

M = metal

Me = methyl, CH_3-

mnt = maleonitriledithiolate, 2,3-dimercapto-2-butenedinitrilate(2-), -SC(CN)C(CN)S-

n = integer

Ph = phenyl, C_6H_5-

Pr = propyl, C_3H_7-

pz = pyrazolyl, cyclo-$C_3H_3N_2$-

R = alkyl

thf = tetrahydrofuran

X = halide, F^-, Cl^-, Br^-, I^-

List of Numbered Compounds

1a-m. $[\mathrm{Ir(NHNHC_6H_3G)(CO)(PPh_3)_2]BF_4}$

2. $\mathrm{IrH(CO)_2(PPh_3)_2}$

3. $\mathrm{IrH(CO)(PPh_3)_3}$

4a-e. $[\mathrm{Ir\{N_4(C_6H_4G)_2\}(CO)(PPh_3)_2]BF_4}$

5a-f. $[\mathrm{IrA(NHNC_6H_3G)(CO)(PPh_3)_2]BF_4}$

6. $[\mathrm{IrCl_2(CO)(N_2C_6H_4\text{-}2\text{-}NO_2)(PPh_3)_2}]$

7. $[\mathrm{IrH_2(CO)_2(PPh_3)_2]BF_4}$

8. $[\mathrm{IrH_2(CO)(PPh_3)_3]BF_4}$

9a-b. $[\mathrm{Ir(CO)(NNC_6H_4G)_2(PPh_3)_2]BF_4}$

10a-d. $\mathrm{Ir(NHNC_6H_3G)(CO)(PPh_3)_2}$

11. "$\mathrm{Ir(NHNHPh)(CO)(PPh_3)_2X}$"

12. $\mathrm{Ir(NNC_6H_3G)(CO)(PPh_3)_2X}$

13. $[\mathrm{Ir(NH_2NHC_6H_3G)(CO)(PPh_3)_2X]BF_4}$

14a-e. $[\mathrm{Cp_2WH(NNHC_6H_4G)]A}$

15a-e. $[\mathrm{Cp_2W(NH_2NC_6H_4G)]A}$

16. Decomposition product of 15

17. Insoluble decomposition product of 15

18. $[\mathrm{Cp_2W(NH_2NHC_6H_4G)](BF_4)_2}$

19. $[\mathrm{Cp_2Mo(NH_2NC_6H_4G)]BF_4}$

20. Decomposition product of 19

21. $[\mathrm{Cp_2Mo(NHNC_6H_4G)_2](BF_4)_2}$

22a-b. $[\mathrm{Cp_2Re(NHNC_6H_4G)]BF_4}$

23. $\mathrm{Cp_2Re(NNC_6H_4\text{-}4\text{-}OCH_3)}$

24a-c. $\mathrm{ArSC(CN)C(CN)SAr}$

Chapter I

Diazo Complexes of Transition Metals

A. Introduction

There is considerable activity and interest currently in the area of metal diazo complexes. This work has been stimulated by several things, but greatest among these is a desire to understand processes of facile fixation of dinitrogen, a worthwhile goal by any account.[1]

Enzymatic fixation of dinitrogen produces ammonia, with no detected intermediate or coproduct:[2]

$$N_2 + 6e^- + 6H^+ \rightarrow 2NH_3.$$

A chemical model system based on tungsten or molybdenum also reduces dinitrogen largely to ammonia rather than hydrazine,[3] and a postulated mechanism for this model does not involve a hydrazine intermediate, but generation of ammonia via $M{=}NH\text{-}NH_2$ and $M\text{-}NH\text{-}NH_3$ species.[3a] A second current proposal involves reduction of N_2 to N_2H_2 and then disproportionation and decomposition to give nitrogen, some hydrogen, and either hydrazine, which would be further reduced,[4] or possibly ammonia.[5] Our understanding of the relevant chemistry is so scanty at this point that new results can easily have a significant impact on such proposals.

In our studies cleavage of the N-N bond has not been prominent, so we shall be concerned with the four-electron reduction and increased valency of each nitrogen atom from N_2 to NH_2NH_2, or actually the comparable series from ArN_2^+ to $ArNHNH_2$. (See page xiv for a listing of symbols used throughout the thesis.) The intermediate members are unstable as free compounds, but complexation to a metal markedly increases their stability and allows their isolation and identification. Because this work involved every step in the series of complexes M-N_2 to M-NH_2NHAr, it will be convenient to introduce briefly each type of complex in turn. The substituted and unsubstituted species of a given diazo parent are easily and appropriately discussed together.

Since the free ligands were largely unknown, naming of their complexes has been unusually nonstandardized, even in recent literature. The names used below for each ligand follow the recent IUPAC recommendation for nitrogen compounds.[6] The terms diazo and aryldiazo have been used generically, to cover all N-N species. If numbering is done systematically, the nitrogen designated N(1) may change as M-N(1)-N(2)-Ar is stepwise protonated. To avoid confusion we have numbered all complexes in the way just shown; the aryl-bound nitrogen is N(2).

B. N_2 Complexes

At one end of the series are metal-dinitrogen complexes. Though over 100 dinitrogen complexes have been identified,[7] in most of them the N_2 is stable except to simple dissociation. Substitution for N_2 can be used synthetically,[8,9] but the dearth of chemistry other than nitrogen loss has served to calm some of the early excitement with this ligand. The lack of current reviews, after an earlier flurry,[10] is a symptom of this change.

Though there is evidence for side-on bonding of N_2 to a metal,[11] dinitrogen generally binds end-on to simple metal complexes. The crystal structure of trans-$RhCl(N_2)\{P(2\text{-}C_3H_7)_3\}_2$ is purported to show side-on bound N_2.[12] However the complex was described as centrosymmetric due to disorder and the bond lengths and thermal parameters are peculiar, so it seems that the crystal structure results are not unequivocal. The reported medium intensity of the infrared N≡N stretching frequency does not seem consistent with side-on bonding, and N_2 in the closely related compound trans-$RhH(N_2)\{P(C_4H_9)_2Ph\}_2$ was earlier found to be bound end-on.[13] Structures with bridging, side-on N_2 are conglomerates with lithiums at the end-on positions.[14] Such species[15] are sufficiently different from the other well characterized transition metal complexes that this sort of side-on bonding will not be further considered in this discussion.

Dinitrogen binds to metals of groups 4A through 8 in their low oxidation states.[7] The critical bonding interaction is apparently delocalization of electrons from the metal into nitrogen π-antibonding orbitals.[16] This lowers the N-N stretching frequency and slightly increases the N-N bond distance.[13] When large, this shift of electron density makes the ligand more negative than carbonyl, as in the analogous complexes $ReCl(L)(PMe_2Ph)_4$ where L = N_2 or CO.[17] Then the terminal nitrogen of M-N≡N is moderately basic. Adducts with a wide range of Lewis acids have been identified.[18] These binuclear N_2-bridged species are linear.[19]

The bridged complex, $[(Cp_2Zr(N_2))_2N_2]$, reacts with acid to generate hydrazine,[20] as does the related species $[(Cp_2Ti)N(MgCl)=N(Cp_2Ti)]$.[15] Ammonia is the principal reduced product of the hydrolysis of $Cr_2N_2Mg_4Cl_2(thf)_5$ or $\{Cr(dppe)_2\}_2N_2$.[21] There is only one other type of isolated[22] dinitrogen complex which produces ammonia upon treatment with acid, $[M(N_2)_2(PPh_{3-n}R_n)_4]$, where M is tungsten or molybdenum.[3] Studies of these latter have been extraordinarily fruitful[23] for several research groups, with a series of intermediates (vide infra) isolated as well as complete reduction to ammonia accomplished.

C. NNH-Type Complexes

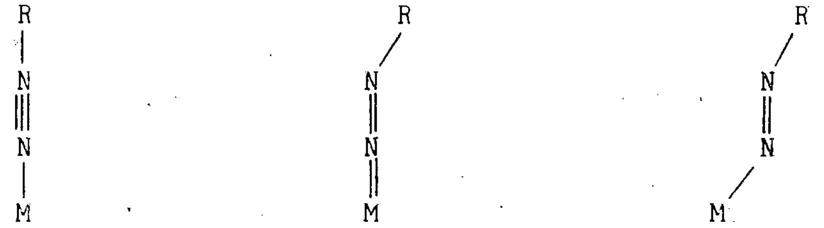
Complexes of the diazenide function, $G\text{-}N{=}N^-$,[24] are sufficiently numerous to have deserved a recent review,[25] so they shall not be dealt with in detail here. Though the title of the review notes a close aryldiazenido-nitrosyl structural analogy, the analogy has not been tremendously useful because many syntheses of complexes of one ligand are not convertible to the other, and the most interesting chemistry of each is not shared by the other. The most common reagent for nitrosyl synthesis has been NO gas. Typical syntheses of aryldiazenido complexes, on the other hand, involve diazonium cations, by substitution for a carbonyl or phosphine, or by simple (oxidative) addition to a basic metal.

Isolated examples of syntheses of alkyl-, acyl-, aryl-, aroyl-, and unsubstituted diazenido complexes from hydrazines,[26-31] phenyl(trimethylsilyl)diazene,[32,33] and diazoalkanes[34] have been reported. A few dinitrogen complexes have been found to react to form diazenido complexes, members of the series mentioned at the end of Section B. For example $W(N_2)_2(dppe)_2$ reacts with a large excess of HX to give the diprotonated species, $WX_2(N_2H_2)(dppe)_2$,[35] which can be neutralized to $WX(NNH)(dppe)_2$.[36] Attempted addition to $W(N_2)_2(dppe)_2$ of one mole of acid to form the diazenido complex directly is unsuccessful since protonation occurs at the metal under these conditions.[23] A mechanism rationalizing this has been described,[37] which also relates to the formation of acyl- and aroyl-diazenides of the form $ReCl_2(NNCOR)(PMe_2Ph)_3$ and $WCl(NNCOR)(dppe)_2$.[38] The analogous alkyldiazenido complexes are formed from $M(N_2)_2(dppe)_2$ (M= Mo,W) generally by irradiating solutions in the presence of chloro-,[39] bromo-,[38] or iodo-alkane.[40] The mechanism of formation is thought to involve an excited state of the metal complex with increased electron density at N_2,[41] or homolytic cleavage of the R-X bond in $RXMo(N_2)(dppe)_2$.[42]

Aryldiazenido complexes are known for metals of groups 6A through 8 except for technetium and nickel. The crystal and molecular structures of several examples have been determined. In mononuclear complexes the most common geometry is singly-bent,[25] with MNN greater than 171°

and NNR in the region of 120°.[43] Variations of these angles toward the all-linear[44] or doubly-bent[45] forms have been reported and examples of each extreme are known.[46-49] Diazenide can also function as a bridging ligand, generally by binding two metals to N(1).[27,33,50,51] An example of the alternate N(1),N(2)-bridging has also been found.[52]

Figure I-1. Geometries Established for Bound Diazenide



Linear RN_2^+ Singly-bent RN_2^+ Doubly-bent RN_2^-

N^1-Bridging RN_2^- N^1,N^2-Bridging RN_2^-

The singly bent form is analogous to the majority of nitrosyls, in which NO acts as a three-electron donor. In the case of nitrosyls there is no obvious structural indication of the hybridization of the oxygen. But with aryldiazenides the location of R off the N-N axis suggests approximate sp^2 hybridization of N(2). The doubly-bent form, corresponding to bent, one-electron-donor nitrosyls, occurs in complexes where the electron density is better stabilized in the ligand than at the metal.

There has been speculation that the catalytic properties of some of the nitrosyl complexes arises from the ability of linear NO to act as a relatively stable electron pair holder as it becomes bent in reaction intermediates.[53] Though diazenido complexes have a similar potential, it does not appear they will be as useful as nitrosyls because they tend to decompose too readily. For example, $PtCl(NNPh)(PEt_3)_2$ decomposes to the phenyl complex during chromatography on alumina, and evolves dinitrogen rapidly upon dissolving in chloroform.[54] And $ReCl_2(NNCOR)(PMe_2Ph)_3$ reacts at room temperature with excess ligand and methanol to give $ReCl_2(N_2)(PMe_2Ph)_4$.[55]

In general the chemistry of no metal-diazo species has been well developed, but more papers are now dealing with this aspect in addition to synthesis and structure. A novel reaction of diazenido complexes is exchange with NO^+. The equilibrium

$$[ArNN\text{-}Fe(CO)_2(PPh_3)_2]^+ + NO^+ \rightleftarrows ArNN^+ + [ON\text{-}Fe(CO)_2(PPh_3)_2]^+$$

is found to lie to the right.[56] The diazenide in $ReCl_2(N_2COPh)(PPh_3)_2$ is replaced by NO giving $ReCl_2(NO)(PPh_3)_2$.[28]

The reaction most looked for involves addition of acids to the basic nitrogens. Many, but not all, diazenides can be protonated, as exemplified by the reactions:[57]

$[Ru(NNAr)(CO)_2(PPh_3)_2]BF_4 + HBF_4 \rightleftarrows [Ru(NHNAr)(CO)_2(PPh_3)_2](BF_4)_2$ Eq. I-1

and $[Fe(NNAr)(CO)_2(PPh_3)_2)]BF_4 + HBF_4 \rightarrow$ N. R. Eq. I-2

With hydrohalic acids addition of a halide to the metal may occur at the same time.[57]

$[Ru(NNAr)(CO)_2(PPh_3)_2]^+ + HI \rightleftarrows [RuI(NHNAr)(CO)_2(PPh_3)_2]^+$ Eq. I-3

Though reduction at a diazenide function by dihydrogen occurs, the expected M-NH-NHR has not yet been isolated, because such species are reactive enough to undergo further changes: (i) decompositon to metal hydride,[58] (ii) reduction,[59] (iii) addition of HX,[32] or (iv) loss of HX.[60] Reduction by H_2 using forcing conditions or by stronger reducing agents, e.g. borohydride, produces metal hydrides.[61,62]

D. NHNH- and NNH_2-Type Complexes

Protonation can occur at either nitrogen of a complexed diazenide. A diazene complex, M-NH=NR, is produced if the metal-bound nitrogen is the basic site. Diazenes make up the largest class of diazo ligands, for it includes such stable members as azobenzenes and pyrazolines. A recent review has discussed the metal complexes of such dialkyl- and diaryl-diazenes.[63] Their bonding to metal clusters, as indicated by crystal structures, is quite complex. It is hoped that an appreciation of the ligand-cluster interactions may lead to development of more efficient catalysts for commercial reduction of dinitrogen.

Complexes of the more stable, disubstituted diazenes are formed directly from the free ligand. This is not true for less substituted diazenes because the uncoordinated species are too unstable to handle easily, though monosubstituted alkyl- or aryl-diazenes have been detected in dilute solution,[64] and can be stabilized in a $(CuCl)_x$ polymer.[65,66] Complexes of diazene and its monosubstituted derivatives must be made from an already metal-bound precursor, but once synthesized such ligands are stabilized by interaction with the transition metal.

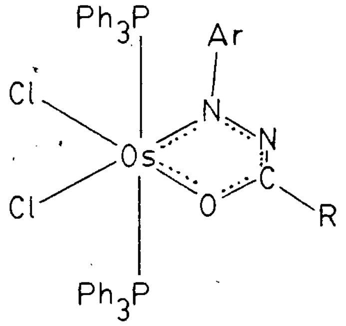
Monoaryldiazenes are most commonly synthesized from diazenido species by protonation (Eq. I-1,3) or insertion into a metal hydride bond.[54]

$$\begin{tikzcd}
PtCl(NNPh)(PEt_3)_2 + H^+ \arrow[dr] & \\
& [PtCl(NHNPh)(PEt_3)_2]^+ \\
PtClH(PEt_3)_2 + PhNN^+ \arrow[ur] &
\end{tikzcd}$$

Eq. I-4

Analogous syntheses of monoalkyldiazenes have not been developed because there is no generally available method of obtaining the prerequisite alkyldiazenides. The addition of a diazoalkane to a metal hydride has given a chelating diazene after rearrangement, $[CpMo(CO)_2\{NHNC(CO_2Et)COH\}]$.[67]

Synthesis of diazene complexes by oxidation of complexes of substituted or unsubstituted hydrazines has been developed spottily. It has been used to prepare bridging diazene,[68-70] but the non-bridging ligand may possibly be oxidized more easily than the starting hydrazine complex and so be unobtainable this way.[71] Acyl- and aroyl-hydrazines have been used repeatedly to make N,O-bonded chelates, e.g.[72]



which contain a delocalized diazene.[72-74] PhNLiNLiPh reacts with $(Ph_3P)_2NiCl_2$[75] and similar palladium and platinum species[76] to form π-bound diazene complexes such as $(Ph_3P)_2Ni(PhNNPh)$ with elimination of LiCl. Diazenides have been isolated from phenylhydrazine, as noted above. The reaction of hydrazine itself with transition metal complexes has produced complexes of nitrides, hydrides, or dinitrogen rather than diazene.[77]

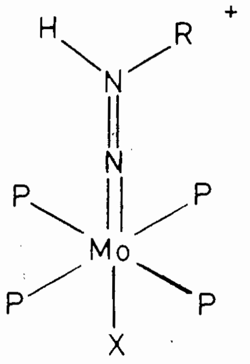
Reactions of coordinated diazenes include substitution by CO,[62] extrusion of N_2,[63,78] reduction by borohydride to metal hydride,[62] aerial oxidation to dinitrogen,[79] and generation of hydrazine by (i) disproportionation,[5] (ii) reduction by H_2,[32,60,80,81] or (iii) reaction in a protic solvent with oxidation of the metal.[82,83]

The hydrazide(2-) ligand, NNRR', is an isomer of diazene. The one example outside Mo, W and Re chemistry is $(Me_2NN)Cu_3Cl_3$.[84] The synthetic route to this and other examples[29,85] involves reaction of

1,1-disubstituted hydrazine. The group 6a and 7a species are also formed by protonation or alkylation of a dinitrogen complex (vide supra) or by attack of an electrophile, e.g. H^+ or Et_3O^+, at an 18-electron, singly-bent diazenido complex:[29]

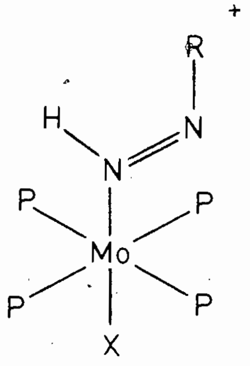
$$Mo(NNPh)(S_2CNR_2)_3 + HBF_4 \rightarrow [Mo(NNHPh)(S_2CNR_2)_3]BF_4. \quad \text{Eq. I-5}$$

This early transition metal chemistry is distinct since singly-bent diazenido complexes of group 8 metals have not been protonated at N(2) (though they may bend and be protonated at N(1), vide supra). The formation of complexed hydrazido(2-) rather than diazene can be partially rationalized, since the latter would have a 16-electron metal configuration without coordination of an additional donor ligand,



Hydrazido Complex

Metal has 18 electrons



Diazene Complex

Metal has 16 electrons

but this does not explain why a hydrazido form is still generally preferred in the presence of excess halide, which could coordinate to the diazene form to give an 18-electron configuration. (See further I-1.) Equations I-1 and I-3, and reference 38.)

The substance $[MoF(NNH_2)(dpe)_2](BF_4)$ has been shown to react like phenylhydrazine in condensing with a ketone to from a hydrazone-type ligand, N_2CRR'.[86] Other reactions of the hydrazido(2-) complexes include isomerization to diazenes,[23] deprotonation,[38] and reduction to amines.[87]

E. $NHNH_2$-Type Complexes

There have been only a few brief reports of hydrazido(1-) complexes, so each can be mentioned here. Most examples arise from hydrazine chemistry. For instance, a bridging, unsubstituted hydrazide $[\{Pt(PPh_3)_2(NHNH_2)\}_2]Cl_2$ forms from cis-$PtCl_2(PPh_3)_2$ and hydrazine.[30] The species $[CpMoI(NO)(NHNMe_2)]$, which is monomeric in chloroform, was isolated from $Cp_2MoI(NO)$ and Me_2NNH_2. It readily loses dimethylhydrazine to form a bridged hydrazido(2-) complex of known structure.[85] A dihapto-phenylhydrazine, $[CpMoI(NO)(N_2H_3Ph)]BF_4$, is formed by acidification of a compound now formulated as $[CpMoI(NO)(N_2H_2Ph)]_n$. The structure of the latter is not clear but may be a bridging hydrazide(1-) bound at both nitrogens.[88]

There are two reports of hydrazido complexes produced from other sources. $Cp_2MoH(NRNHR)$ was isolated from insertion of an azo compound with strongly electron-withdrawing R functions into Cp_2MoH_2.[89] And, in the series of products from group 6 dinitrogen complexes, reaction of $W(N_2)_2(PMePh_2)_4$ with HCl in dichloromethane produces

$WCl_3(NHNH_2)(PMePh_2)_2$. This reaction is quite sensitive to change of solvent and phosphine; in most cases addition of acid generates diazenes or ammonia.[82]

It is noteworthy that this series of complexes derived from $W(N_2)_2(PR_nAr_{3-n})_4$ does not extend to a hydrazine derivative, though small yields of free hydrazine have been found with the ammonia produced in reactions of the various species with methanolic sulfuric acid.[3] The stability of $(OC)_5CrN_2H_4$ to reduction argues against mechanisms involving reduction of a complexed (unidentate) hydrazine during enzymatic nitrogen fixation.[69] Furthermore since free hydrazine is not detectible in active extracts, nor is it reduced by the enzymes studied,[2] a pathway through free hydrazine is barely tenable. Thus the chances that the $W(N_2)_2(PR_nAr_{3-n})_4$ chemistry is indeed a good model increases as other possibilities are eliminated.

F. NH_2NH_2-Type Complexes

Hydrazine and substituted hydrazines, the other end of this series of diazo species, have long been known as ligands but their chemistry, like that of disubstituted diazenes, has not been well developed. Two relatively recent reviews have dealt with the transition metal chemistry of hydrazine[77] and substituted hydrazines.[76] This area was considerably extended with the preparation of neutral complexes of terminal and bridging hydrazine.[69,70,85,89,90]

The chemistry of complexed hydrazines is intimately connected with the more oxidized diazo species. Several hydrazine complexes have been produced by reduction of diazenes with dihydrogen. It was such a reduction in the case of his platinum aryldiazenes that led Parshall to title a paper "An Inorganic Analogue of Nitrogen Reductase."[80] While analogy to the enzymatic process now appears weak, such reactions remain of interest for possible large scale synthesis of substituted hydrazines.

Conversely, oxidation of substituted hydrazine complexes is believed to involve hydrazides[91] or diazenes,[64] though these have rarely been isolated.[69] Syntheses of diazenido complexes from hydrazines have been more successful, but only for group 6[26,29] and 7[27] metals.

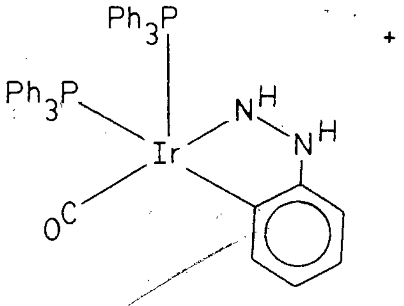
G. Thesis

At the time my research program was initiated, there were relatively few aryldiazenido complexes known. It was not readily apparent which synthetic methods would be generally useful. The objective was to prepare aryldiazenide analogues of well-studied nitrosyl complexes to compare the structure and bonding of the two, with the idea that such data might help lead to catalytic use of aryldiazenides (vide supra). But the study envisioned could not be carried out as synthesis was a great problem.

As time passed it became clear that one of the generally useful synthetic procedures is insertion of aryldiazonium into a metal hydride bond.[25] We have extended the application of this method by using d^8-cobalt group hydrides and group 6 and 7 hydrides because in each case the chemistry of diazonium addition/insertion products appeared to be novel. Thus the research reported in the following chapters is highlighted by reactions of metal hydrides with diazonium salts.

Hydridocarbonyltris(triphenylphosphine)iridium and hydridodicarbonylbis(triphenylphosphine)iridium react with diazonium salts to produce orthometalated compounds, **1**. The hydridic and ortho-aryl protons appear in the product bound to nitrogens:

$IrH(CO)(PPh_3)_2L + PhNN^+ \rightarrow$



where L = CO or PPh_3.

The diazo ligand is thus one of the rare hydrazido complexes identified and is both quite different from and better characterized than the other examples. Synthesis, solid state structure, and spectroscopy of these hydrazides is discussed in Chapter II.

Syntheses of arylhydrazido complexes **1** were accompanied by formation of several by-products. These are identified in Chapter III. By neutralization of the acidic arylhydrazido complexes, one can obtain neutral, orthometalated aryldiazene complexes of iridium(I). The arylhydrazido complexes react with hydrohalic acids as well. The chemical properties of 1, including this acid and base chemistry, is also covered in Chapter III, which is concluded with the experimental description of all this iridium chemistry.

Biscyclopentadienyldihydridotungsten reacts at low temperatures with one mole of benzenediazonium salt to give an insertion product, $[Cp_2WH(NNHAr)]^+$, which has an arylhydrazide(2-) rather than an aryldiazene structure. As solutions of this cation are warmed, it isomerizes to a hydrazide(1-) bound at both nitrogens. With change in the central metal to molybdenum or rhenium the reactions still occur without nitrogen evolution, but the products are different; they appear to be aryldiazenes. Presentation of this work composes Chapter IV.

It was discovered that diazonium ions attack sodium bis(maleonitriledithiolato)ferrate(III) at the sulfur atoms to give uncomplexed thioethers. This work is covered in Chapter V.

An appendix describes and discusses a variety of reactions including: i) attempted insertion of diazonium ion into the metal-metal bond of iron carbonyls, ii) attempted reactions of metal nitrosyls with anilines, and iii) attempted synthesis of $[Ru(NH_3)_5NNPh]^{3+}$.

Chapter II

Orthometalated Arylhydrazido Complexes of Iridium

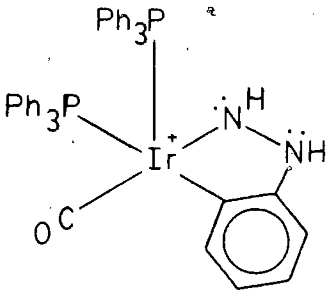
A. Introduction

Our interest in the possibility of obtaining products by reaction of benzenediazonium salts with $IrH(CO)(PPh_3)_3$, **3**, was directly stimulated by earlier studies on $IrCl(CO)(PPh_3)_2$. When this widely used chloroiridium compound, Vaska's complex, reacts with diazonium salts in ethanol or 2-propanol, the alcohol is stoichiometrically oxidized to the corresponding aldehyde or ketone.[60] As this was reminiscent of alcohol acting as a hydride donor in the synthesis of some metal hydrides,[92] the reaction of an iridium hydride suggested itself as a way to isolate intermediates not obtainable from Vaska's complex. But an earlier report of the reaction of **3** with a diazonium salt was not encouraging as no product had been isolated.[32]

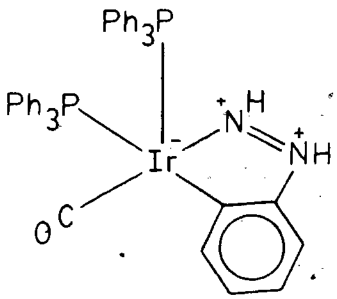
The synthetic breakthrough was the realization that if one mole of diazonium salt were 'lost' reacting with triphenylphosphine,[93] then two moles of diazonium salt would be required for each mole of $IrH(CO)(PPh_3)_3$. Using this proportion of $2\text{-}O_2NC_6H_4N_2BF_4$, [illegible] Nicholas Farrell isolated a deep purple-red iridium complex, **1b** (See Table II-1 for a listing of complexes **1**.), with infrared absorption at 3280 and 2000 cm^{-1}. With other diazonium salts the crude, dried reaction mixtures showed inter alia these infrared absorptions, but the analogous products were not separated. As an extension of work on other metal hydrides , I hoped to develop the reaction chemistry of **1b**, the correct formulation of which had not been established.

An X-ray crystal structure determination, done largely by Dr. Roger Cobbledick, was helpful in the elucidation of the structure of **1b**, showing the presence of an orthometalated aryl ring. Combined with spectroscopic data, this allowed the compounds to be identified as variously substituted (arylhydrazido-*C*^{6},*N*^{1})carbonylbis(triphenylphosphine)iridium tetrafluoroborates, **1**. (To avoid the attendant confusion of using different numberings for the reactant diazonium salts and their products, we consistently number the diazo-substituted position $C^{1'}$ and the metal-substituted (orthometalated) site C^6.)

Details of the crystal structure are indicative of the electronic structure and so the dimensions of the cation can be compared with parameters expected for the predominance of resonance extremes such as forms **1'** and **1"**.



1', hydrazidoiridium (III)



1', diazeniumiridium (I)

Thus, the discussion which follows below, of both the crystal structure and the spectroscopic and chemical data, is directed toward definition of the most reasonable, useful picture of bonding in the complex.

B. Synthesis

The set of arylhydrazido complexes $\underset{\sim}{1}$ has been prepared from three different iridium complexes: $IrCl(CO)(PPh_3)_2$, $IrH(CO)_2(PPh_3)_2$, $\underset{\sim}{2}$, and $IrH(CO)(PPh_3)_3$, $\underset{\sim}{3}$. The last of these was generally used, and will be described first.

1. From $IrH(CO)(PPh_3)_3$

Reasonable yields were obtained by simultaneously adding both a solution of $\underset{\sim}{3}$ in benzene or toluene and a propanone solution of two moles of the diazonium salt. At low temperatures (253 K) the normal color change to intense red still occurred, but more slowly. Since there seemed no advantage to working at low temperatures, all syntheses were run at room temperature. The propanone/benzene or propanone/toluene reaction mixtures were first evacuated to dryness under vacuum (stripped). In the case of propanone/toluene a useful separation occurred thereby, in that the desired arylhydrazido complex generally oiled out of solution later than other iridium-containing products and so could be partially purified by decanting.

Pure microcrystalline samples of $\underset{\sim}{1}$ were then obtained by addition of a small volume of methanol acidified by addition of aqueous fluoroboric acid. Spontaneous solidification of the oil occurred upon stirring in this solvent and other products were sufficiently soluble or slow-to-solidify that they did not interfere. When the separation of pure solid was slow, addition of ether and hexane followed by brief evacuation did facilitate the process. Elemental analyses for the hydrazido complexes isolated are given in Table II-1.

The solids isolated by recrystallizations of **1** from mixed solvent systems such as alcohol/ether/hexane upon cooling were always mixtures of **1** with iridium diazene complexes **5**, $[Ir(NHNC_6H_3R)F(CO)(PPh_3)_2]BF_4$. Thus the arylhydrazido complexes obtained as described in the last paragraph were not successfully recrystallized except that crystals suitable for x-ray diffraction could be grown by slow solvent evaporation (Done for **1b** and d; see further Section II-C.) from pure samples of **1**. The presence of even a small amount of **5** in a sample of **1** was apparent in the infrared from a carbonyl absorption near 2040 cm^{-1}. (See Figure II-3.) This seemed to be a more sensitive test of the purity of a sample of **1** than analysis. All analyses in Table II-1 were done on samples with no distinct absorption above ca. 2000 cm^{-1}.

The crude isolates from the reaction of each monosubstituted benzenediazonium salt showed infrared absorptions typical of **1**. Thus, even when the arylhydrazido complex could not be separated (**1c**,e,g,j, and m), there was evidence that it was normally produced. Orthometalation is apparently blocked with 2,6-F_2- or 3,5-Me_2-benzenediazonium salts since no hydrazide was detected in these cases.

Table II-1. Elemental Analyses of Orthometalated Arylhydrazido Complexes, $[Ir(NHNHC_6H_3G\text{-}C^6,N^1)(CO)(PPh_3)_2]BF_4$.

No.	R	Percent Composition						Yield
		Found			Calculated			%
		C	H	N	C	H	N	
1a	H	54.8	4.06	2.77	55.1	3.87	2.99	13[b]
1b	$2\text{-}NO_2$	52.8	3.74	4.09	52.6	3.59	4.28	11[b]
1c	$2\text{-}CF_3$	Not purified						-
1d	2-F	54.2	3.74	3.02	54.0	3.69	2.93	11[b]
1e	2-Br	Not purified						-
1f	$2\text{-}OCH_3$	54.6	3.98	2.85	54.6	3.96	2.89	24[b]
1g	$3\text{-}NO_2$	Not purified						-
1h	3-F	Not analyzed						<2[b]
1i	$3\text{-}CH_3$	49.9	4.04	2.93[a]	55.5	4.02	2.94	
1j	$4\text{-}NO_2$	Not purified						-
1k	4-F	54.0	3.73	2.89	54.0	3.69	2.93	5[b], 17[c], 43[d]
1l	$4\text{-}CH_3$	55.1	4.12	2.93	55.5	4.02	2.94	34[c]
1m	$4\text{-}OCH_3$	53.6	4.00	2.38	54.6	3.96	2.89	63[d]

a) Average of three analyses of same product. Carbon values vary widely (± 3 %).

b) From $IrH(CO)(PPh_3)_3$.

c) From $IrH(CO)_2(PPh_3)_2$.

d) From $IrH(CO)_2(PPh_3)_2$, unrecrystallized.

Initial crystallization from different solvent pairs was tried but was never successful, at room temperature, with slow cooling to 268 K, or at 198 K. Synthesis using other solvents was also unproductive. For example, an ether suspension of hydride **3** treated with diazonium salt slowly produced a green solution until toluene was added, after which the reaction appeared to proceed normally, giving red products. In a dimethylformamide solution/suspension, the hydride again reacted quite slowly. No normal products were identified except $IrH_2(CO)(PPh_3)_3BF_4$, produced here in 50 % yield, distinctly higher than usual (c.f. Chapter III).

2. From $IrH(CO)_2(PPh_3)_2$

Only one mole of diazonium salt per mole of **2** was used. Otherwise the reaction and isolation procedures were similar to those above. Development of redness in the reaction mixture is not much slower with **2** than with **3**. Since the red is ascribed to **1** (and/or tetrazene complex, see Chapter III), the loss of CO from the dicarbonyl hydride is not especially difficult. No bubbling of CO was apparent.

3. From $IrCl(CO)(PPh_3)_2$

Addition of propanone at below 273 K to an intimate mixture of solid $IrCl(CO)(PPh_3)_2$ and an equimolar quantity of solid 2-nitrobenzenediazonium tetrafluoroborate, followed by addition of ethanol and warming produced a mixture containing **6**, $[IrCl_2(CO)(NNC_6H_4\text{-}2\text{-}NO_2)(PPh_3)_2]$,[49] and the hydrazido complex,

1b. The former is insoluble in propanone/ethanol and so could be filtered off, but **1b** in the dried filtrate was still contaminated. The contaminant, apparently **6** by infrared absorption, could be extracted into benzene, but not efficiently. Though this synthesis plays an important role in the elucidation of the mechanism of reaction of Vaska's complex,[94] there were no advantages that would have made this the preferred method of synthesis of **1**, so it was abandoned.

The hydrazido complexes isolated are crystalline, red solids. The colors of samples are somewhat varied. With nitro substitution the color is shaded toward violet and with less electronegative groups toward orange. The complexes dissolve moderately well in polar solvents (ethanenitrile, chloroform, dichloromethane, propanone, ethanol, methanol) and are insoluble in ethanoic acid, benzene, toluene, ether, hexanes, and water. Their narrow proton magnetic resonance absorptions (FWHM = 2 Hz) indicate complexes **1** are diamagnetic.

C. Crystal and Molecular Structure

Under a slow flow of N_2, evaporation of mixed solvents propanone and methanol from an HBF_4-acidified solution of 1b left well-formed, elongated platelets. To remove the involatile fluoroboric acid, the crystals were washed four times with glacial acetic acid and three times with benzene, then vacuum dried. Once free from solvent the solids are stable to air under fluorescent lighting at room temperature for months.

Oscillation, Weissenberg, and precession photographs were taken using a rod-shaped crystal chosen for similar dimension of the short axes, approximately 0.3 x 0.15 x 0.1 mm. Accurate determination of unit cell dimensions, data collection, and solution of the crystal structure were then done by Dr. Cobbledick on a Picker FACS-1 automatic four-circle diffractometer. Unit cell dimensions were determined from a least-squares refinement of the setting angles for ten strong reflections of the $MoK\alpha_1$ peak with $2\theta > 27^\circ$. Intensity data were collected with the long crystal a axis approximately coincident with the ϕ axis of the diffractometer, using a graphite monochromator and a scintillation counter with pulse-height analysis. Relevant data are shown in Table II-2.

A Patterson synthesis allowed positioning of the iridium and phosphorus atoms. Further non-hydrogen atoms were determined from electron-density difference syntheses. Full-matrix least-squares refinement was used throughout.[95] Anisotropic temperature factors were included for the iridium, phosphorus, fluorine and nitro-oxygen atoms.

Table II-2. Crystal and X-Ray Data.

Formula: $C_{43}H_{35}BF_4IrN_3O_3P_2$

M = 982.8

Crystal system: monoclinic

Space group: $P2_1/c$

Unit cell dimensions: a = 1092.1(3) pm
b = 2012.5(7) pm
c = 1806.1(5) pm
β = 97.78(2)°

Z = 4 V = 3.933 nm^3

ρ_o = 1.65 g cm^{-3} (by flotation)

ρ_c = 1.659 g cm^{-3}

λ(Mo K_{α_1}) = 70.926 pm

μ(Mo K) = 37.5 cm^{-1}

T = 298 ± 2 K

Reflections = 2504 $(0<2\theta<35^\circ)$

Observed reflections $(I > 2.3\,\sigma(I))$ = 2069

Total parameters = 275

R = 0.0415

Most phenyl and aryl hydrogen atoms were apparent from the electron-density difference syntheses so these were added at calculated positions with a C-H bond length of 97 pm. With R reduced to 0.045, peaks in the difference map remained in chemically reasonable positions for N(1)- and N(2)-bound hydrogens. These were then included in the fixed positions indicated by the difference map peaks. In two final cycles of refinement, no parameter shifted by more than 0.15 standard deviation. The greatest residual electron density was a peak 147 pm from the iridium, roughly toward N(1).[96]

Tables II-3 and II-4 list respectively selected interatomic distances and angles. Displacements of atoms normal to the most pertinent least-squares planes is reported in Table II-5. In a full report the reflection amplitudes and calculated structure factors, atomic coordinates, and equations for least-squares planes have been listed,[97] so these are not included herein.

The crystal structure consists of discrete, cationic, pentacoordinate, iridium complexes linked though weak N-H···F bonds to tetrafluoroborate anions. A diagram illustrating one ion pair is shown in Figure II-1. Figure II-2 gives the packing in the unit cell. There is no unusually close intercomplex separation; the shortest such contacts are to the nitro group (O(2)···C(2), 321; O(2)···H(1), 258 pm) and the tetrafluoroborate ion (F(1)···C(4), 324; F(1)···H(3), 249 pm), each from a phenyl of an adjacent complex. The packing shows a

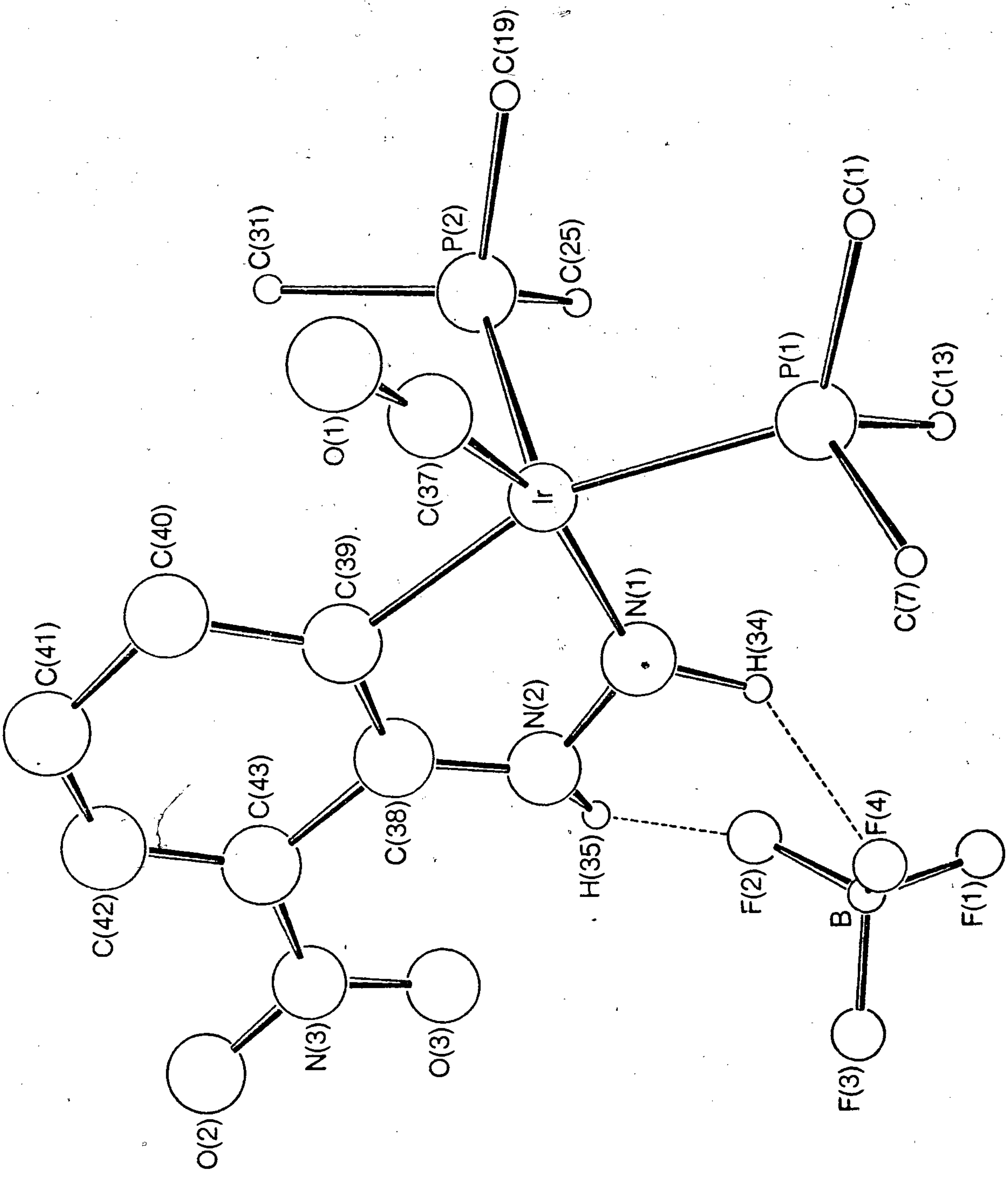


Figure II-1. A perspective View of a Molecule in

$[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$

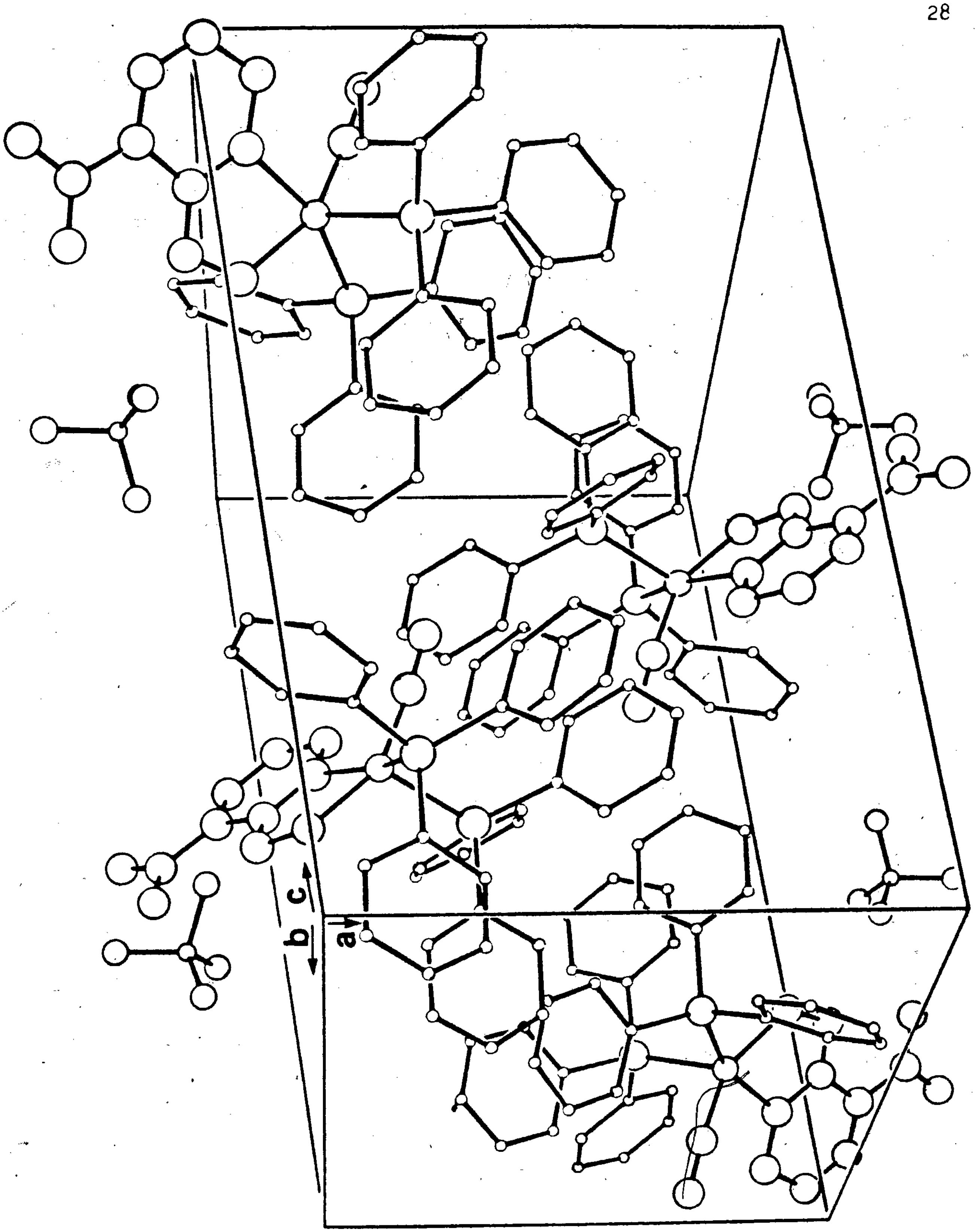


Figure II-2. Molecular Packing in a Unit Cell of

$[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$

Table II-3. Selected Interatomic Distances in pm[a] for $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$.

Ir-P(1)	240.2(4)	Ir-P(2)	232.2(4)
Ir-C(37)	175.0(12)	Ir-N(1)	191.2(10)
Ir-C(39)	209.1(13)	P(1)-C(1)	184.8(12)
P(1)-C(7)	180.8(13)	P(1)-C(13)	180.8(13)
P(2)-C(19)	183.7(13)	P(2)-C(25)	181.1(13)
P(2)-C(31)	184.0(13)	Mean phenyl C-C	137.8(5)
B-F(1)	132.4(26)	B-F(2)	128.6(26)
B-F(3)	137.5(25)	B-F(4)	140.0(27)
N(1)-N(2)	138.8(13)	N(2)-C(38)	130.2(15)
C(38)-C(39)	135.7(17)	C(39)-C(40)	140.3(17)
C(40)-C(41)	141.8(18)	C(41)-C(42)	130.0(18)
C(42)-C(43)	130.0(18)	C(38)-C(43)	149.0(18)
C(43)-N(3)	144.4(20)	N(3)-O(2)	122.9(18)
N(3)-O(3)	122.4(17)	C(37)-O(1)	121.5(12)
N(1) F(4)	295	N(2) F(2)	287
N(1)-H(34)	110	N(2)-H(35)	97
H(34) F(4)	203	H(35) F(2)	196
N(2) O(3)	263	H(35) O(3)	220

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[a] Estimated standard deviations in parentheses.

Table II-4. Selected Interatomic Angles in Degrees[a] for $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$.

P(1)-Ir-P(2)	99.5(1)	P(1)-Ir-C(37)	96.6(4)
P(1)-Ir-N(1)	88.6(3)	P(1)-Ir-C(39)	159.8(4)
P(2)-Ir-C(37)	93.0(4)	P(2)-Ir-N(1)	112.7(3)
P(2)-Ir-C(39)	99.4(4)	C(37)-Ir-C(39)	89.6(5)
C(37)-Ir-N(1)	152.6(5)	C(39)-Ir-N(1)	77.5(5)
Ir-P(1)-C(1)	121.4(4)	Ir-P(1)-C(7)	110.3(4)
Ir-P(1)-C(13)	112.4(4)	Ir-P(2)-C(19)	113.9(4)
Ir-P(2)-C(25)	113.9(5)	Ir-P(2)-C(31)	114.8(4)
F(1)-B-F(2)	113.8(24)	F(1)-B-F(3)	106.2(22)
F(1)-B-F(4)	110.6(21)	F(2)-B-F(3)	112.3(23)
F(2)-B-F(4)	108.1(22)	F(3)-B-F(4)	105.4(20)
Ir-N(1)-N(2)	119.1(8)	N(1)-N(2)-C(38)	113.2(11)
N(2)-C(38)-C(39)	119.0(13)	N(2)-C(38)-C(43)	126.3(14)
C(39)-C(38)-C(43)	114.5(13)	C(38)-C(39)-Ir	110.0(10)
Ir-C(39)-C(40)	125.3(10)	C(38)-C(39)-C(40)	123.6(13)
C(39)-C(40)-C(41)	115.8(13)	C(40)-C(41)-C(42)	122.2(15)
C(41)-C(42)-C(43)	122.6(16)	C(42)-C(43)-C(38)	121.0(15)
C(38)-C(43)-N(3)	117.8(15)	C(42)-C(43)-N(3)	121.1(16)
C(43)-N(3)-O(2)	117.5(18)	C(43)-N(3)-O(3)	120.5(18)
O(2)-N(3)-O(3)	121.9(20)	Ir-C(37)-O(1)	175.3(10)
N(1)-H(34)···F(4)	139	N(2)-H(35)···F(2)	155

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[a] Estimated standard deviations in parentheses.

Table II-5. Deviations from Least-squares Planes Calculated for $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$.

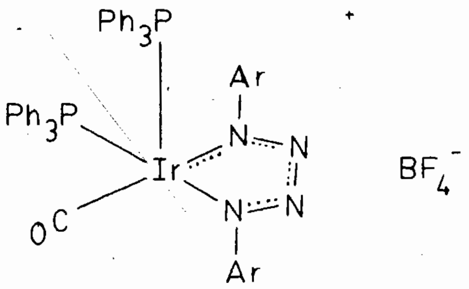
Atoms Defining Plane	Deviations From Plane in pm	χ^2
P(1),N(1),C(37),C(39)[a]	P(1) 0.3; N(1) -3.8; C(37) -4.0	48.11
	C(39) 6.0; Ir 36.8	
C(38),C(39),C(40), C(41),C(42),C(43)	C(38) 1.8; C(39) -1.6; C(40) 1.5	6.04
	C(41) -1.0; C(42) 1.0; C(43) -1.4	
	N(1) -4.6; N(2) -0.2; Ir 1.4	
N(1),N(2),C(38),C(39)	N(1) 0.1; N(2) -0.2; C(38) 0.4	0.14
	C(39) -0.2; Ir 9.4; H(34) -11	
	N(35) 25	

[a] These atoms are not coplanar.

distinct pattern along the a axis of alternating non-polar (phenyl) and polar (BF_4^-, NO_2, NH) layers. Otherwise the packing is not noteworthy.

The polar functions all seem weakly hydrogen bonded.[98] Approach of each of two tetrafluoroborate fluorines to the two hydrazido NH groups is close enough to indicate weak hydrogen bonding.[99] Furthermore, since the dihedral angle between the aryl ring and the nitro substituent is only 7°, O(3) is in close contact with N(2), suggesting a bifurcated hydrogen bonding system[100] about the N(2)-bound hydrogen.

The coordination geometry about each iridium is best described as an irregular square-based pyramid. The apex is occupied by one of the two triphenylphosphine ligands, so the phosphorus atoms are mutually cis. The apical Ir-P bond of 232.2(4) pm is significantly shorter than the equatorial Ir-P bond of 240.2(4) pm. This is a larger difference than that of 4.2 pm in the structure of carbonylbis(triphenylphosphine)-(1,4-di-p-fluorophenyltetrazene)iridium tetrafluoroborate, 4c,[101]



4

although the mean of the two bond lengths is identical in the two complexes. The phenyl rings are all bonded normally. One phenyl of the basal phosphine occupies the region trans to the apical phosphine, but the closest approach to the iridium of an ortho hydrogen is over 300 pm, which implies that no significant interaction is involved.

There are two idealized geometries for five-coordinate complexes, trigonal-bipyramidal (TBP) and square pyramidal. These have quite similar total electronic energies so that predictive calculations have been difficult. Examples of square pyramidal geometry are most common for d^6-transition metal systems, which are in fact calculated to be more favored with respect to their TBP isomers than any other d^n-system.[102] Thus the gross geometry about iridium suggests that the metal is effectively iridium(III) as in resonance form **1'**. If one considers the alternative d^8-iridium(I) electronic structure of **1"**, the highest energy d-orbital, $d_{(x^2-y^2)}$, would be empty and the $d_{(z^2)}$-orbital filled. This would in turn require that the axial Ir-P bond be longer than the basal Ir-P bond; the opposite is in fact true.

It is noteworthy that other five-coordinate, square-pyramidal, d^6-complexes have an axial ligand, such as NO^-,[48,103,104] alkyl,[105] or acyl, with a strong trans influence. In **1b** the group with the strongest expected trans influence, the coordinated aryl, is not axial but trans to the basal phosphine. So this structure and the closely comparable one of the tetrazene **4** are exceptional. One rationalization is that the bite of the chelate ($\angle$CIrN = 77.5(5)°) is small enough to appreciably destabilize the complex if the aryl group were axially disposed. If the bite requires the chelate to coordinate in the base, it follows that the phosphines must be cis to one another in spite of their bulk.

Recent crystal structure data[106] for Ir(III)-P separations fall in the range 232 - 242 pm with only one exception, $IrH_3(PPh_3)_3$. The Ir(I)-P distances vary generally from 227 to 233 pm, though there are several exceptions. Here again, the structure of **1b** is more consistent with an Ir(III) formulation than Ir(I). Furthermore one may note that the axial phosphine of **1b**, with no trans ligand, is at the short end of the range of Ir(III)-P bond lengths while the basal phosphine, with a strongly trans-lengthening aryl group opposite to it, is at the long end of the same range. The difference in Ir-P bond lengths can thus be seen as a simple function of the trans ligand.

The iridium-carbonyl bond is short and the carbonyl C-O bond is the longest recently reported for an iridum complex.[106] Discussion of this is deferred to the next section.

The basal atoms are the carbonyl carbon, the triphenylphosphine phosphorus, the aryl carbon, and N(1) of the chelating arylhydrazide. These are only approximately planar. As usual, the iridium atom lies out of the least-squares plane toward the axial phosphorus, 36.8 pm.

The iridium coordination strongly indicates that the metal is appropriately described as d^6-iridium(III), and that resonance form 1″ does not dominantly contribute to the actual electronic structure. We will see that the geometry of the hydrazide ligand supports this conclusion. Though the complexes are properly named as iridium(III) hydrazides, there was no particular reason to expect that the name would be as appropriate as it is.

The four, arylhydrazide ligand atoms in the metallocycle are coplanar, but tipped so that the iridium is 9.4 pm out of this plane, toward the axial phosphine. To give perspective to the bonding in the metallocycle, Table II-6 presents the bond lengths in the arylhydrazido complex along with the corresponding bond lengths in related complexes.

The arylhydrazido 1 and tetrazene 4 complexes show distinct parallels in the metallocycle as well as in metal stereochemistry. The similarities between the two ligands are apparently more critical than the differences. They are both ligands of ambiguous electronic structure, found to be coordinated as dianions with charge formally on the ligating atoms, one of which is an N trans to the carbonyl. In both structures the Ir-N bond trans to the carbonyl is shorter than the bond trans to phosphine.

The greatest difference between the orthometalated arylhydrazide ligand in 1b and orthometalated aryldiazenes, e.g. in 5, is the long N-N bond length of the former. The additional 10 pm N-N separation

Table II-6

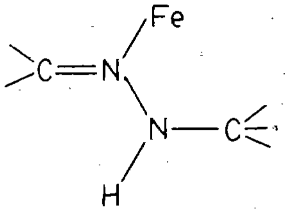
Bond lengths in pm Useful for Comparison with Those of $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$.

Compound	Ir-N	N-N	N-C(aryl)	C-C of metallocycle	Ir-C(aryl)	Ref
$[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$	191.2(10)[a]	138.8(13)	130.2(15)	135.7(18)	209.1(13)[b]	-
$[Ir\{(C_6H_4\text{-}4\text{-}F)_2N_4\}(CO)(PPh_3)_2]BF_4 \cdot C_6H_6$	194.1(13)[a]	140.0(16)	[127.0(16)][c]	[135.0(16)][c]	[197.1(10)][d]	101
$[Ir(NHNC_6H_3\text{-}4\text{-}F)Cl(CO)(PPh_3)_2]BF_4 \cdot (CH_3)_2CO$	204(3)[a]	128(3)	139(3)	138(4)	201(3)[e]	164
$[Ir(NHNC_6H_3\text{-}4\text{-}OCH_3)Cl_2(PPh_3)_2] \cdot CHCl_3$	199.0(7)[e]	127.2(9)	137.6(12)	140.9(12)	201.1(8)[e]	135
$[IrCl_2(N_2C_6H_4\text{-}2\text{-}NO_2)(CO)(PPh_3)_2] \cdot 2(CH_3)_2CO$	205(4)[e]	119(4)	147(4)	-	-	49
$[PtCl(NH_2NHC_6H_4\text{-}4\text{-}F)\{P(C_2H_5)_3\}_2] \cdot BF_4$	-	143.6(11)	140.8(11)	-	-	195

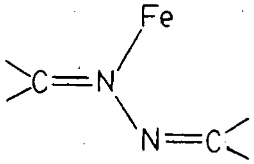
[a] Trans to CO [b] Trans to P [c] Distance of anologous bond [e] Ir-N bond trans to P

[e] Trans to Cl [f] Trans to F

implies a sharp decrease of net N-N bonding in the hydrazide. Though the N-N distance in 1b is not as long as a typical hydrazine single bond, as shown by comparison with the bond length in the platinum hydrazine complex included in Table II-6, some of the difference is likely due to more sp^2-character (c.f. section II-E) in each hydrazide nitrogen compared to the hydrazine. Lengths of the N-N bonds of

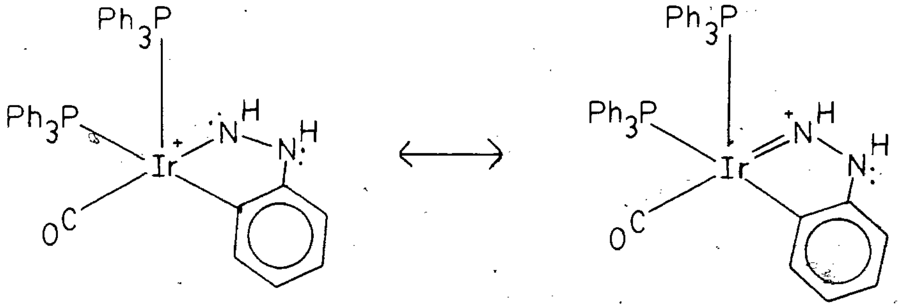


and



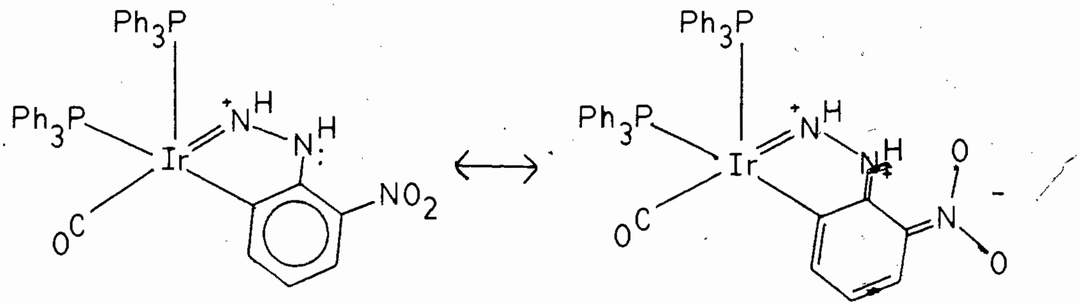
in macrocyclic ligands[107] are identical to the N-N bond length in the hydrazido complex 1b. So it appears that there is little N-N multiple bond character in this complex, as depicted by structure 1'.

Other bond lengths, however, do not all agree with those one would expect if bonding were well-described by 1'. First, the Ir-N bond is significantly shortened compared to the diazenes. The most reasonable mechanism for this effect is donation of the N(1) lone pair of structure 1' onto the iridium, as in resonance form 1'''.



1' 1'''

This would reduce repulsion with the lone pair on N(2), equalize the atom charges, and give iridium an 18-electron valence system. Second, the N(2)-C(aryl) bond across the metallocycle from the iridium is moderately shortened, suggesting some multiple bond character. With 2-nitro substitution it is reasonable to postulate some importance to an orthoquinone-like resonance form for the aryl ring:



1'''

The aryl C-C bond lengths, though not uniform, show no distinct alternating pattern. There appears to be no appreciable Ir-C(aryl) multiple bond character, as this bond is quite long.

In summary, the crystal structure indicates that the complex is one of an iridium (III) hydrazide with the lone pairs on each nitrogen moderately delocalized, but in such a way that the N-N bond order is little increased above that of a single bond. While none of the resonance forms is dominant (or negligible), 1''' would appear to give the best single picture of bonding.

D. Infrared Spectra

Though the infrared spectra were not interpreted conclusively until the crystal structure was available, it is satisfying that information from vibrational spectroscopy does appear completely consistent with the bonding picture derived from the structure.

The absorptions occurring in virtually all the complexes 1a-1h are: 3280 m, 3058 wm, 2000 vvs, 1481 m, 1435 s, 1311 w, 1185 wm, 1162 wm, 1118 s or sh, 1090 vvs, 1055 s, 999 m, 744 m, 693 vvs, 617 vw, 519 vvs, and 421 cm^{-1} wm. See Figure II-3 for example. Many of these are due to coordinated triphenylphosphine. The tetrafluoroborate absorptions are at about 1055 and 519 cm^{-1}. The latter is coincident with a phenyl band.

The single most characteristic peak is the medium intensity band, generally near 3280 cm^{-1}, due to NH stretching. Its intensity is rather high, as expected with hydrogen bonding.[108] The band is quite broad to lower frequency due to the presence of a second band, not generally resolved, at ca. 3230 cm^{-1}. With isotopic substitution of ^{15}N at N(1) the absorption of 1k dropped from 3282 to 3275 cm^{-1}. Thus the higher frequency absorption is assigned as primarily N(1)-H stretching and the lower frequency, broader band as primarily N(2)-H stretching. The energy of these absorptions is about the same as that of the NH stretch of 1,2-diphenylhydrazine,[109] imines,[110] and coordinated or free diazenes (3500-3120 cm^{-1}, see Table II-8). It is

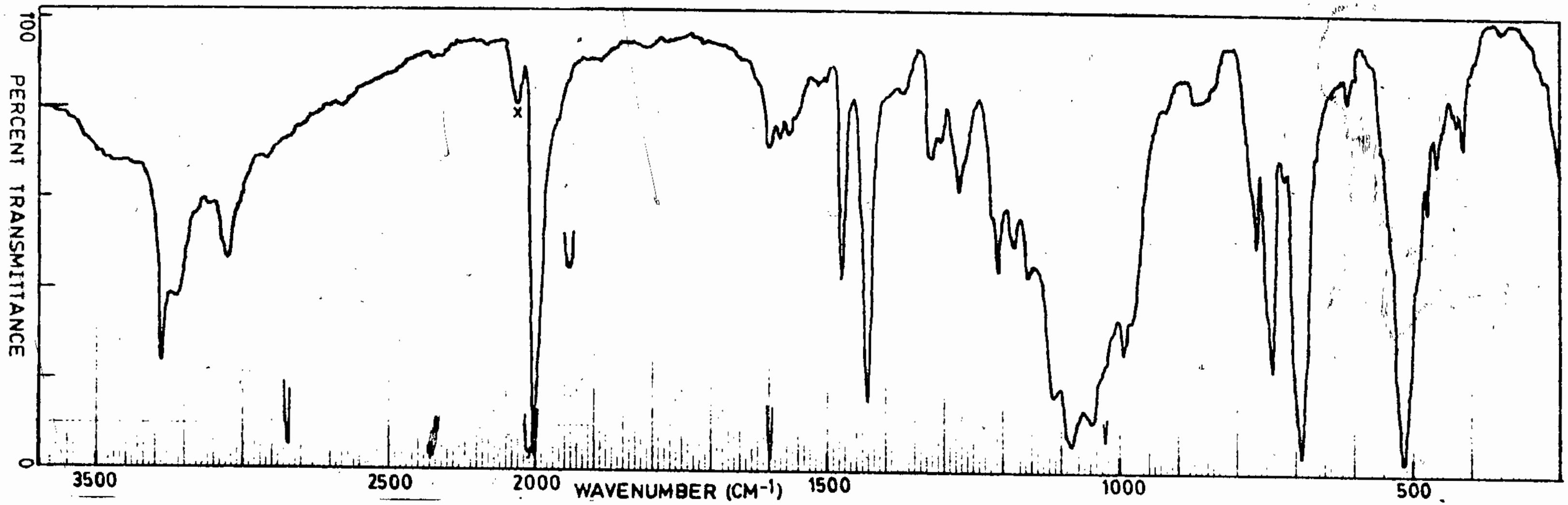


Figure II-3. Infrared Spectrum of $[Ir(NHNHC_6H_3\text{-}3\text{-}F)(CO)(PPh_3)_2]BF_4$.

Peak marked with X due to $[IrF(NHNC_6H_3\text{-}3\text{-}F)(CO)(PPh_3)_2]BF_4$ contaminant.

higher than that of ammonium and imine salts.[111] Like the crystal structure results, this argues against influence of resonance form 1'' since the N(2)-H stretch for such a structure would be expected at a lower frequency than the observed bands. Both structures 1' and 1''' are compatible with the infrared since coordination of the nitrogen to a metal does not lead to an NH frequency lowering. (See Table II-8.)

The very strong absorption at 2000 cm^{-1} is clearly the CO stretch. This band is not as useful here as it generally is. It is not by itself indicative of the presence of 1 in crude isolates because the dihydridoiridium cations also absorb at this energy (c.f. Chapter III). Second, there is little variation in the absorption frequency with change in aryl substitution. Since 2000 cm^{-1} is the frequency at which the spectrometers used change gratings or prisms, the uncertainty of measurement of this peak is especially high and precludes correlating frequency with changes in aryl substitution.

Finally, the position of the absorption is between those for closely related Ir(I) and Ir(III) monocarbonyl complexes. Without other information this datum would remain ambiguous. But we have seen that the solid state structure is characteristic of Ir(III). The question becomes why is the carbonyl stretching frequency so low in these cationic arylhydrazidoiridium(III) complexes. The principle component in M-CO bonding and in lowering ν(CO) is interaction between filled metal d orbitals and the π^*-orbitals of $-C{\equiv}O$.[112] As this interaction increases CO antibonding increases, lengthening the CO distance and lowering ν(CO), while M-C bonding increases, shortening this bond.

As noted above, the C-O separation in 1 is the longest in any recently reported iridium carbonyl structure by nearly three standard deviations. And except for the structure of $IrCl(CO)\{P(C_6H_4\text{-}2\text{-}CH_3)_3\}_2$, which has high uncertainties due to disorder,[113] 1 has the only Ir-CO bond length less than 180 pm. Clearly, the x-ray results are consistent with the low carbonyl stretching frequency observed, though the displacement of the carbonyl carbon toward the metal is unrealistically large.[114]

Both these structural and infrared effects might result from good overlap of π-type orbitals along the O(1)-C(37)-Ir-N(1)-N(2) chain. The novelty of the bonding in this five-atom system is supported by the aforementioned shortness of the Ir-N bond trans to carbonyl in both 1 and 4.

Other bands in the spectrum are generally weaker than those noted above. Absorption characteristic of the substituents is generally clear. A medium strength absorption at 1213 (3-F and 4-F) or 1234

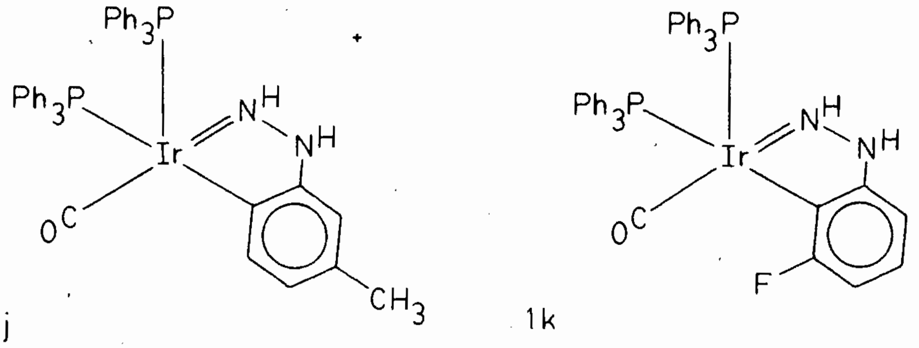
cm^{-1} (2-F) is assigned to ν(aryl-F) in 1d,h,k. Strong absorptions at 1253 and 1029 cm^{-1} in 1f are due to asymmetric and symmetric C-O-C stretching. 1b has no band of intensity appropriate to $\nu_{asym}(NO_2)$ in the region 1600-1500 cm^{-1}; a band at 1496 cm^{-1} is assigned to this mode. This indicates an unusually high degree of conjugation with a good electron donating group, which requires that the nitro group lie close to the plane of the aryl group. The crystal structure does support this high degree of conjugation. Absence in 1b of the weak intensity band found at 1311 cm^{-1} in the spectra of differently substituted 1 suggests that in 1b this is coupled with the $\nu_{sym}(NO_2)$; the peaks at 1332 (m) and 1285 (s) are thus assigned as coupled modes with intensity due to an extremely intense $\nu_{sym}(NO_2)$ component.

The out-of-plane bending modes of C(aryl)-H are seen to change upon orthometalation, but because some bands are masked by the more intense phenyl absorptions any consistent assignment is seriously hampered. It was primarily for this reason that orthometalation was not realized before the crystal structure. We note that others have not been able to discuss their infrared evidence for orthometalation using group frequencies of out-of- plane bending modes.[115-117] It would seem that extension of the group frequencies noted for alkyl- and halo-substituted benzenes[118] to aryl-metal compounds is generally not valid,[119] though it is possible in some cases.[60] This should not detract from the use of these infrared bands in simply detecting orthometalation;

the absorptions characteristic of the unmetalated ring are lost and new ones arise when metalation occurs.

The limited number of derivatives lends uncertainty to correlations of frequency patterns with substitution patterns, but some generalizations and inferences can be made. Ortho-substituted benzenediazonium salts give 1,2,3-substituted aryl groups once orthometalated. This is seen in 1d and f as a shoulder near 765 cm^{-1}, shifted to 793 cm^{-1} in the nitro analogue 1b. A band at 772 cm^{-1} in 1h suggests that orthometalation of the meta-fluorophenyl group occurs so as to give a 1,2,3-substitution pattern as well. (Figure II-3) In complex 1i, the meta-methyl analogue, the shift of this band to 800 cm^{-1} is so large that the alternative 1,2,4-substitution is implied.

Figure II-4. Stereochemistry of meta-Substituted Hydrazides as Suggested by Infrared Absorption in the range 900-700 cm^{-1}.



1j 1k

The 1,2,4-substitution necessarily obtained by orthometalation of a para-substituted phenyl group is characterized by a band just below 800 cm^{-1} in 1k and 1. All complexes 1 have weak, and often broad, absorption bands in the range 925-840 cm^{-1}.

There is no evidence for infrared absorption corresponding to an NN stretching mode. With isotopic substitution there was no shift noted, even in aryl frequencies with which ν(N-N) might be coupled.[120] This would indicate that ν(N-N) occurs below the region of ν(C-C aryl) and might be Raman active. Most samples placed in the Raman beam decomposed quite visibly immediately. A sample of **1d** however survived well enough to allow recording of its spectrum, which was poor because of fluorescence. The relatively strong peak observed at 1329 cm^{-1} is tentatively assigned to ν(N-N). The assignment is consistent with resonance forms **1'''** and **1'** since it suggests little multiple bond character between the nitrogens.

A Raman band at 1348 cm^{-1} in the orthometalated diazo complex $Ir(C_6H_4N{=}NPh)ClH(PPh_3)_2$ has been assigned to ν(N-N).[121] In the orthometalated Ir(III) aryldiazenes $[IrCl(NHNC_6H_3R)(CO)(PPh_3)_2]BF_4$, N=N stretching has been assigned to infrared bands at 1410 or 1440 cm^{-1} depending on the position of substituent R.[60] Commonly ν(N=N) has been assigned at frequencies above 1450 cm^{-1}.[122]

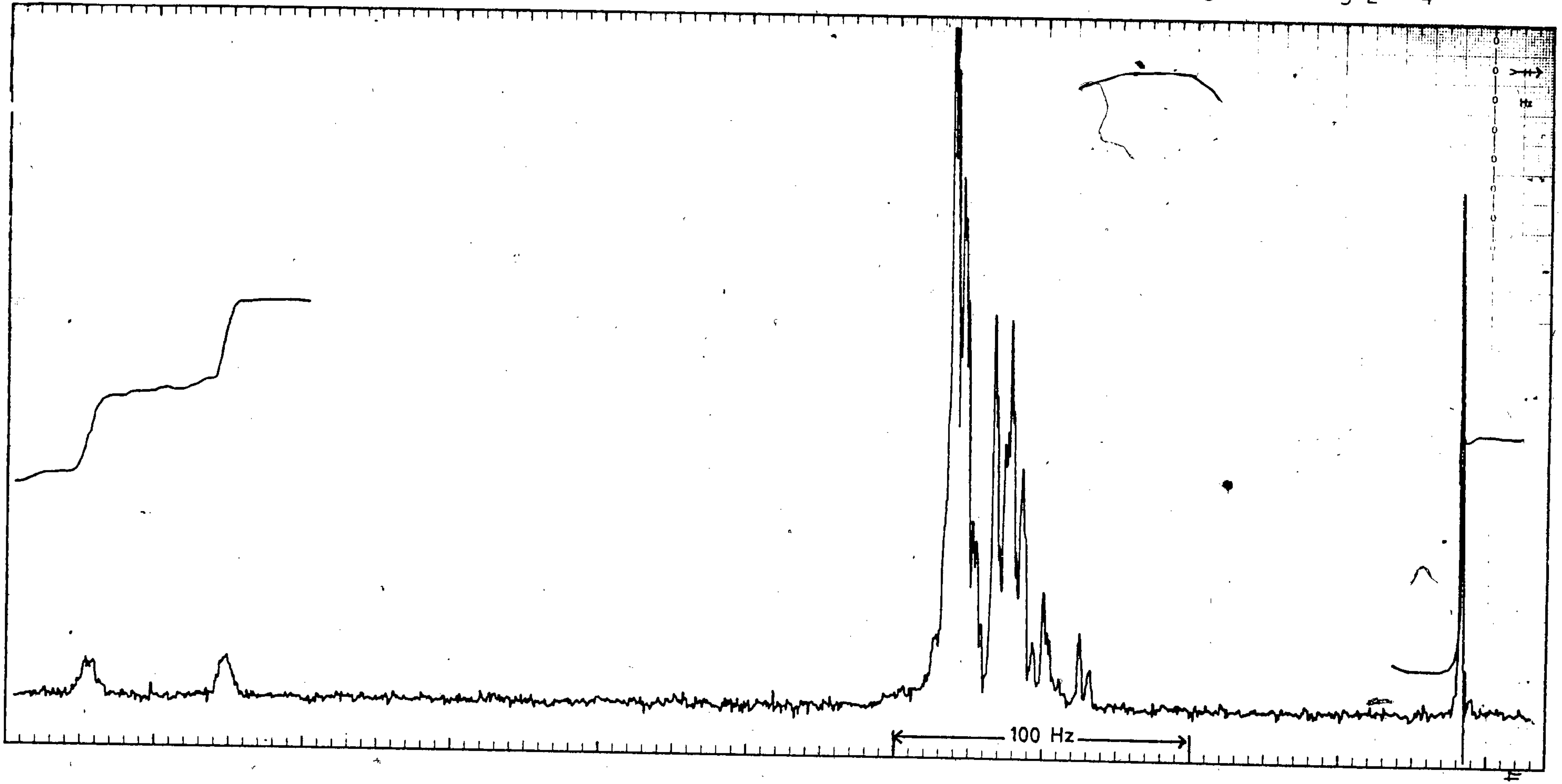
The infrared of **1g**-$^{15}N(1)$ does not allow identification of an iridium-nitrogen stretching mode either. One band is apparently shifted from 551 to 533 cm^{-1} with the ^{15}N-substitution, but since many of the $^{14}N(1)$-arylhydrazides do not absorb near 550 cm^{-1}, its assignment as ν(Ir-N) in **1g** is unreasonable.

E. Nuclear Magnetic Resonance Spectroscopy

The 30 hydrogens of the triphenylphosphine generally obscure the signals of the orthometalated aryl ring, so ^1H-nmr is not useful for identifying orthometalation in the hydrazides 1. However information obtained about the nitrogen-bound hydrogens is especially valuable. The nmr spectra allow the definite location on different nitrogens of these two hydrogens. Their low-field resonance indicates that there is appreciable delocalization about this NH-NH group.

The aryl and phenyl region extends from δ 7.8 to 6.4, though most of the intensity lies within two bands at δ 7.5-7.3 and 7.2-6.9 in deuteropropanone or 0.15 ppm lower in $CDCl_3$. (See Figure II-5.) In some compounds phenyl resonances have been found to separate sufficiently to allow assignment, based on integration, of peaks due to ortho-H at different chemical shift from meta- and para-protons.[123] This appears to apply reasonably well to 100 MHz spectra of 1. The effect of the nitro group of 1b shifts all aryl signals downfield so that the upfield band integrates to 12.0 hydrogens, as expected solely from ortho-phenyl protons. The spectral pattern in the upfield band of 1b, a sawtooth pattern of pairs of peaks (These are recorded, as "doublets", in Table II-7 because the pattern does appear consistently.), is duplicated in the other hydrazides, though integration suggests some aryl hydrogen intensity occurs in this range with the less electronegative substituents. The pattern, presumably A and A' out of an AA'BB'CX system, could not be transformed into a set of coupling constants, the $^3J_{PH}$ of which might have been informative.

Figure II-5. 100 MHz Proton Magnetic Resonance Spectrum of $[Ir(NHNHC_6H_3\text{-}4\text{-}OCH_3)(CO)(PPh_3)_2]BF_4$.



The pattern of resonances in the downfield band is not as consistent as the upfield peaks. Integration suggests that most aryl intensity is found here. The residual $CHCl_3$ in the $CDCl_3$ solvent absorbs in this region as well so the integrations reported in Table II-7 omit the phenyl region when done in deuterochloroform. In instances of occurrence of an apparent pattern of peaks separated from the bulk of aryl and phenyl absorptions, tentative assignments have been made. (See Table II-7.)

The hydrazido complexes **1** all showed absorptions from two hydrogens bound to different nitrogen atoms well downfield from the phenyl absorptions. The position of these was quite sensitive to solvent. This sensitivity is obvious for the NH of coordinated diazenes and hydrazine as well. (See Table II-8.) Upon addition of 1 drop H_2O to **1b** both NH signals disappeared faster than a duplicate spectrum could be run (0.1 h). With **1d** the methoxy hydrogens serve as a useful internal reference for relative integrated intensity, which is 1.0:1.0:3.0 for N(2)H : N(1)H:OCH_3. (Figure II-5)

The pmr spectrum of **1g**-$^{15}N(1)$ allowed verification of the assignment as only one of the two NH signals was split, the upfield signal. The slightly broad NH resonances are not significantly sharpened by ^{15}N-substitution so the width arises from the effect of slow exchange more than the ^{14}N quadrupole. A small splitting (J=3 Hz) of the N(2)-H resonance appears rather consistently in both

Table II-7. ^1H-NMR Data for $[Ir(NHNHC_6H_3R)(CO)(PPh_3)_3]BF_4$.

Substituent Solvent	Position[a] (Rel. Peak Height)	Description[b]	[Integ.]	Assignment
1b 2-NO_2	14.1	br s or m, FWHM=10 Hz	[0.6]	N(2)
	12.6	br s or m, FWHM= 9 Hz	[0.6]	N(1)
$(CD_3)_2CO$	8.09	d, J= 8 Hz	[1.0]	3-aryl
	ca. 7.46, 7.36	complex	[20.0]	3-,4-phenyl; 4-,5-aryl
	7.17(5),7.13(2),7.08(3),	apparent d's		2-phenyl
	7.05(5),7.01(2),6.96(3),6.86(1)	J<2 Hz	[12.0]	
	2.77			trace water
	1.09 t & 3.36 in noise	J=7 Hz		trace ether
1b 2-NO_2	14.1	br s or m, FWHM=10 Hz		N(2)
	13.1	br s or m, FWHM=12 Hz		N(1)
$CDCl_3$	8.00	d, J=8 Hz		3-aryl
	ca. 7.33	complex		3-,4-phenyl; 4-,5-aryl
	7.06,6.95,6.87,6.73			2-phenyl
	3.44 q & 1.16 t	J=7 Hz		trace ether
	2.15			trace propanone
1c 2-F	13.81	br s or m, FWHM=14 Hz		N(2)
	13.12	br s or m, FWHM=11 Hz		N(1)
$(CD_3)_2CO$	7.46	complex	[20.6]	3-,4-phenyl; aryl
	7.17(5),7.14(2),7.09(3),	apparent d's		2-phenyl; aryl
	7.05(5),7.02(2),6.97(3),6.80(2)	J<2 Hz	[12.4]	
	3.27 s			trace methanol
	2.72 s			trace water
	2.27 & 0.20 s			?

Table II-7 (continued). ^{1}H-NMR Data for $[Ir(NHNHC_6H_3R)(CO)(PPh_3)_3]BF_4$.

Substituent Solvent	Position[a] (Rel. Peak Height)	Description[b]	[Integ.]	Assignment
1d 2-OCH_3	13.24	br s or m, FWHM=10 Hz	[1.0]	N(2)
	12.26	br s or m, FWHM=11 Hz	[1.0]	N(1)
$CDCl_3$	ca. 7.30	complex		3-,4-phenyl; aryl
	7.03(5),6.95(4),6.91(5), 6.83(3),6.69(2)	apparent d's J<2 Hz		2-phenyl; aryl
	6.42	apparent d, J=8 Hz		3- or 5-aryl
	3.86	s	[3.0]	OMe
1g 4-F	13.25	apparent d, J=3 Hz, FWHM=15 Hz		N(2)
	11.94[c]	br s or m, FWHM=12 Hz		N(1)
$CDCl_3$	7.80	t (d of d), $^3J_{HH}$=9 Hz, $^4J_{HF}$=9 Hz		2-aryl
	ca. 7.32	complex		3-,4-phenyl; aryl
	7.01(7),6.90(8), 6.83(5),6.50(1)	apparent d's J<2 Hz		2-phenyl; aryl
	3.48 q & 1.20 t	J=7 Hz		trace ether
	2.13 s			trace propanone

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a) Reported in ppm downfield from internal tetramethylsilane.
b) Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; FWHM, full width at half maximum.
c) With $^{15}N(1)$: br d, $^1J_{(^{15}NH)}$-84 Hz

$^{14}N^{14}N$ and $^{15}N(1)^{14}N$ complexes and may be due to $^{3}J_{HH}$, though it is not seen for N(1)-H. A $^{2}J_{NH}$ coupling between $^{15}N(1)$ and the H at N(2) might be expected,[122] and could be large if there were a lone pair at $^{15}N(1)$.[124] Its absence is not too instructive.

The large ^{15}N-H splitting and low field chemical shift of **1** deserve more than passing comment because they emphasize the importance of a facet of the electronic structure which the infrared and x-ray data did not, that is the similarity of the environment of each nitrogen with that in diazenes. Previously, workers have rarely given more than a mention to the significance of the PMR of diazene complexes, though the NH chemical shifts are extraordinarily high (above 11.1, see Table II-8) and quite different from values typical for isomeric hydrazido(2-) complexes (below 5.9). What is more, the little they do write is misleading. The high shifts have been improperly reported to (i) indicate the acidity of an aryldiazene NH[68,125] or (ii) be typical of protons at metal-bound nitrogen.[35,126] Point (i) is improper because a proton signal does not shift all that sharply with decrease in electron density,[127] so extreme shifts such as these require that a further effect than (i) be operating. (The pK_a of methyldiazene is thought to be about 18,[64] barely low enough to be called acidic, yet its NH chemical shift is 15.6.) The data on which (ii) is based are apparently limited to diazene $\begin{array}{l}\text{M-NH}\\ \quad\diagdown\text{NG}\end{array}$ and hydrazido(2-) M=N=NHG systems, which differ by far more than merely the site of protonation. Our chelating arylhydrazido(1-) complexes **1** are an exception which disproves this point since both N(1)H and N(2)H absorb at low field.

Table II-8. Collected Infrared and ^{1}H-NMR Spectroscopic Data for N-Bound Hydrogen in Complexed Diazenes and Related Species.

Compound	IR Med	νNH cm^{-1}	NMR Sol	δ_{NH} ppm	$^1J_{NH}$ Hz	Ref
$[Pt(NHNC_6H_4\text{-}4\text{-}F)(CNEt)(PEt_3)_2](ClO_4)_2$	N	3215				81
$[Pt(NHNC_6H_4\text{-}4\text{-}F)(PPh_3)_3](BF_4)_2$	N	3500	T	2.85		58
$[PtCl(NHNPh)(PEt_3)_2]BF_4$	K		T	15.1	77	80
	H		D	14.25	74	122
$[Pt(CCPh)(NHNC_6H_4\text{-}4\text{-}F)(PPh_3)_2]BF_4$			T	13.5		125
$RhCl_3(NHNC_6H_4\text{-}4\text{-}OMe)(PPh_3)_2$			T	11.60	65	32
$[IrCl_2(NHNC_6H_4\text{-}4\text{-}Me)(PPh_3)_3]BF_4$			T	13.98, 13.90		32
$[IrH_2(NHNC_6H_4\text{-}4\text{-}OMe)(PPh_3)_3]BF_4$		3515		13.5		134
$[IrCl(CO)(NHNC_6H_3\text{-}4\text{-}Br)(PPh_3)_2]BF_4$	K	3160	E	14.8	92	60
$[IrH(NHNC_6H_3\text{-}4\text{-}OMe)(PPh_3)_3]BF_4$		3240	t	5.79		134
$IrCl_3(NHC_6H_4\text{-}4\text{-}Me)(PPh_3)_3$			T	13.12		32
$IrCl_2(NHNC_6H_3\text{-}4\text{-}OMe)(PPh_3)_2$	N	3230				134
	N	3350		insol		135
$IrClH(NHNC_6H_3\text{-}4\text{-}OMe)(PPh_3)_2$		3200		5.29		134
$[OsCl(NHNC_6H_4\text{-}4\text{-}Me)(CO)_2(PPh_3)_2]BF_4$			T	11.76		32
$[OsH(NHC_6H_4\text{-}4\text{-}Me)(CO)(PPh_3)_3]BF_4$			T	12.28		32
$OsCl(FBF_3)(NHNC_6H_4\text{-}4\text{-}Me)(CO)(PPh_3)_2$			T	13.78	69	32
$OsCl_2(NHNC_6H_4\text{-}4\text{-}Me)(CO)(PPh_3)_2$			T	13.50	67	32

Table II-8 (continued). Collected Infrared and ^{1}H-NMR Spectroscopic Data.

Compound	IR Med	νNH cm^{-1}	NMR Sol	δ_{NH} ppm	$^1J_{NH}$ Hz	Ref
$[RuCl(NHNC_6H_4\text{-}4\text{-}Me)(CO)_2(PPh_3)_2]BF_4$			T	11.66		32
$[RuCl(NHNPh)(CO)_2(PPh_3)_2]ClO_4$			D	11.75	65	122
$[RuCl(NHNPh)(CO)_2(PPr_2(t\text{-}Bu))_2]BF_4$	N	3378	T	13.57		136
$[Ru(NHNPh\text{-}4\text{-}F)(CO)_2(PPh_3)_2](CF_3CO_2)_2$	N	3130	T	13.65		57
$[RuCl(NHNC_6H_4\text{-}n\text{-}OMe)(CO)(NCMe)(PPh_3)_2]PF_6$ n=4			P	12.10		137
n=3			P	12.65		137
n=2			P	13.96		137
$[RuH(NHNC_6H_4\text{-}4\text{-}Me)(CO)(PPh_3)_3]BF_4$			T	12.05		32
$[RuH(NHNC_6H_4\text{-}4\text{-}Me)(CO)_2(PPh_3)_2]BF_4$			T	12.70		32
$RuCl_2(NHNC_6H_4\text{-}4\text{-}Me)(CO)PPh_3)_2$			T	12.6		32
$RuCl(FBF_3)(NHNC_6H_4\text{-}4\text{-}Me)(CO)(PPh_3)_2$			T	13.10		32
$RuClH(NHNC_6H_4\text{-}4\text{-}Me)(CO)(PPh_3)_2$			T	12.97, 12.62		32
$\{CpMn(CO)_2\}_2N_2H_2$	K	3250	P	14.27		68
$\{CpMn(CO)_2\}NHNH\{Cr(CO)_5\}$	K	3250, 3215	P	15.64 ~~14.74~~		128
$\{CpRe(CO)_2\}_2N_2H_2$	K	3240	P	15.33		138
$[ReCl_2(NH_3)(NNHPh)(PMe_2Ph)_2]Br$	H	2650	T	4.92		139
$\{Mo(CO)_5\}_2N_2H_2$	K	3480, 3240	P	16.5		70
$MoCl_2(NHNCOMe)(dppe)_2$	N	2700, 2640	D	12.0		39
$MoCl_2(NHNCOPh)(dppe)_2$	N	2600		14.1		126
$[MoI(NNHC_8H_{17})(dppe)_2]X$		3275		3.76		141
$[MoBr(NNHEt)(dppe)_2]Br$	H	2860	D	5.9		39
$[MoBr(NNHMe)(dppe)_2]Br$	K		D	8.5		39

Table II-8 (continued). Collected Infrared and ^{1}H-NMR Spectroscopic Data.

Compound	IR Med	νNH cm^{-1}	NMR Sol	δ_{NH} ppm	$^1J_{NH}$ Hz	Ref
$\{W(CO)_5\}_2N_2H_2$		3450, 3250	P	16.4		140
$WF(NNH)(dppe)_2$	N	3365	D	9.60		
$WCl_2(NHNCOPh)(dppe)_2$	N	2650	D	12.5		39
$WCl_2(NHNCOMe)(dppe)_2$	N	2780, 2700	D	13.0	95	39
$WCl_2(N_2H_2)(dppe)_2$	H	3270, 2920	T D	6.50 5.85		35
$[WCl(NNH_2)(dppe)_2]BPh_4$	N	3340, 3230	T D	3.0 3.02		35
$[WBr(NNHMe)(dppe)_2]Br$	d	2980, 2820	T	5.9		39
$[WBr(NNH(t\text{-}Bu))(dppe)_2]Br$	K	3080, 2925	D	3.4		39
$\{Cr(CO)_5\}_2N_2H_2$	K	3480, 3250	P	16.2		69
$\{Cr(CO)_5\}_2N_2H_4$	K	3355, 3300	P	5.45		69
$[CpFe(CO)_2(NH_2NH_2)]BPh_4$	N	3345, 3247, 3217, 3145	D b 	1.73, 0.70 3.52, 3.12		142
NHNMe		3130	E	15.6		143

Key: b, nitrobenzene; D, d_2-dichloromethane; d, dichloromethane; E, d_3-ethanenitrile; H, hexachlorobutadiene; K, potassium bromide; N, nujol; P, d_6-propanone; T, d-trichloromethane; t, trichloromethane.

In searching for a qualitative explanation for the shifts, a good model is clearly the low field resonance of an aldehydic proton. This is due to the neighbor-anisotropy effect,[129] but beyond this little has been developed, historically because Pople did not have good wavefunctions for calculation of carbonyls[127] and pedagogically because the alternate example of an alkynyl hydrogen is easier to present because of its symmetry.[130] Briefly then, the planar carbonyl carbon atom has a greater diamagnetic susceptibility perpendicular to the plane than in it. When averaged over all orientations in space this anisotropy at carbon leads to an increase in the effect of an externally applied magnetic field at the site of the hydrogen. (Compare ethylbenzene with styrene, Table II-9.)

The anisotropy of the carbon susceptibility is due largely to an anisotropy of the paramagnetic part arising from the mixing of the ground state with excited electronic states by the magnetic field.[129] This effect of anisotropy increases with increasing amplitude, at carbon, of the HOMO of the excited state (Compare styrene, N-methylbenzylimine and benzaldehyde, Table II-9.), and is thus greatest for a formyl proton.

With the NH of iminodiphenylmethane three effects giving low chemical shifts come together. A nitrogen-bound hydrogen typically resonates at lower field than its carbon analogue because electron density is displaced away from the hydrogen. (Compare ethylbenzene and

Table II-9. ^{1}H-NMR Resonances[a] of Hydrogens Bound to Planar Second Row Atoms, and Related Species.[b]

Compound	CH Resonances	NH Resonance
$PhCH_2CH_3$	2.53 1.19	
$PhCH_2NH_2$	3.85	1.52
$PhNH_2$		3.32
$PhCH_2NH_3^+$	4.4[c]	ca. 7[c]
PhNH-NHPh		7.49
$PhCH=CH_2$	6.59 cis:5.59 trans:5.11	
$PhCH=NCH_3$	8.11	
$Ph_2C=NH_2^+$		9.56[d]
$Ph_2C=NH$		9.68[d]
PhCH=O	9.97	
MeN=NH		15.6[e]

---

[a] In ppm downfield from tetramethylsilane

[b] Reference 144 unless noted.

[c] Ref. 146

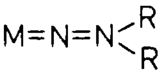
[d] Ref. 145

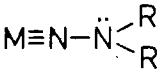
[e] Ref. 143

benzylamine, Table II-9.) The neighbor- anisotropy effect occurs because of the planarity at nitrogen. And finally the paramagnetic contribution is substantial because of the low energy n $\rightarrow \pi^*$ states not possible with carbon analogues. The result is NH resonances in the range of aldehydes. In changing the imine carbon to nitrogen, the HOMO of the excited state should have greater amplitude at the retained nitrogen so the NH proton resonance should be further shifted downfield. Thus it is not unreasonable to find that protons of diazenes (and other -NH= species[131]) absorb above δ 11.5. (See Table II-8. The values below δ 6 would seem to be spurious.)

How do couplings fit into this picture? The expected $^1J_{NH}$ for an sp^2 nitrogen hybrid orbital is about 92 Hz vs. 73 Hz for an sp^3 orbital. A linear relation between hybridization and ^1J can exist if the Fermi contact term is largely responsible for the coupling.[132] However Roberts pointed out that the coupling to π-bonded nitrogen atoms which show large paramagnetic shifts is not necessarily determined largely by Fermi contact interaction. He specifically predicts that "$^1J_{(^{15}NH)}$ for a system such a phenyldiazene should not be determined by the contact term alone."[133] If one may extend his prediction to complexes of aryldiazenes, it seems to be borne out, for the ^{15}NH splittings of coordinated aryldiazenes range from 95 down to 65 Hz. (Table II-8) Thus the wide variation in couplings is seen to be consistent with the large effect of anisotropy at the nitrogen.

The position of NH resonances has recently been the object of more thorough consideration[70] as more data have appeared (See Table II-8). A particularly interesting area of application is in structure elucidation of isomeric diazene, -NRNR', and hydrazido(2-), -NNRR', complexes. From the discussion above we expect the former type to show ^{1}H-NMR absorption for R or R'=H at $\delta > 10$. What about the latter? X-Ray structural studies[141,147] have shown such complexes to have nearly linear M-N-N units. The two obvious bonding configurations which could contribute to the electronic structure are:

(a) 
$M{=}N{=}N{<}^{R}_{R}$

and (b) 
$M{\equiv}N{-}\ddot{N}{<}^{R}_{R}$.

If the complexes are bonded as in (b) then the resonance should be characteristic of an amine. In fact amine-like absorption to high field of δ 9 is typical. Diazene and hydrazido(2-) isomers are differentiated by nmr. (See further Table II-8.)

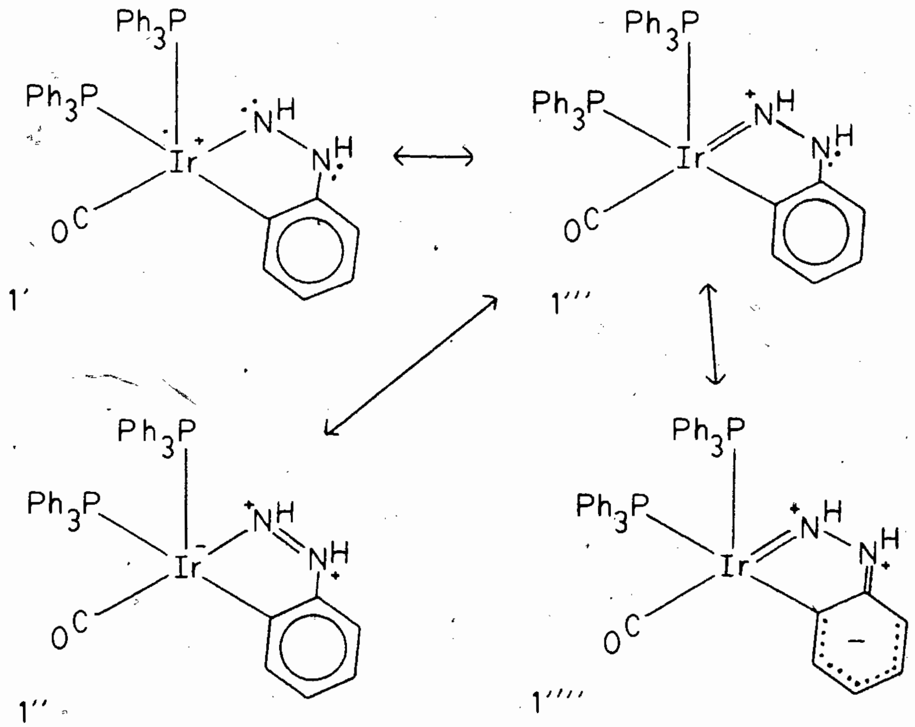
On other evidence the differentiation is not as clear-cut as the last paragraph might lead one to believe. To start with, a central complex to this area of research, $[WCl(N_2H_2)(dppe)_2]^+$, has been reported to contain different N_2H_2 structures with different counterions: hydrazide(2-) with BPh_4^- and diazene with chloride, which is believed to be coordinated.[35] Since the NH chemical shift of $[WCl_2(N_2H_2)(dppe)_2]$ is near 6, this would be an exception to our categorization. Briefly, we believe the diazene postulation to be wrong, that the chloride is loosely bound to a hydrazide hydrogen and that the lack of one-bond ^{15}NH coupling is due to fast exchange. If the lack of coupling were due to exchange between hydrogens of W-^{15}NH=^{15}NH as the authors suggest, then when the motion is frozen out, which occurs near 200K, there should be two different NH doublets. It was reported that there was only one. Since the diazene form has not been found in X-ray crystal structures[141,147] of the spectroscopically similar [MX(NNHR)(dppe)$_2$]X where M= Mo or W, it is quite reasonable that [WCl(NNH$_2$)(dppe)$_2$]Cl should also be a hydrazide(2-).

Secondly, complexes [WCl$_2$(NNHCOR)(dppe)$_2$] do seem to have the diazene structure.[39] The difference between alkyl and acyl complexes is not so large that one could have predicted this change, so the balance controlling which structure is taken is a fairly close one. This is reminiscent of the close balance with rhenium complexes [ReCl$_2$(NNPh)L(PMe$_2$Ph)$_2$] as to whether protonation occurs or not.[139]

Finally, the catagorization above has lumped together complexes which, according to X-ray determinations, span a spectrum of electronic structures between (a) and (b) above.[147] It is rather startling that the chemical shifts of hydrazido hydrogens are as small as they are even though the complexes are probably planar.[141] In terms of the discussion above, the linear W-N-N unit does not appear to have a particularly anisotropic magnetic susceptibility, or at least there is little effect at the proton position in the complexes such as [WBr(NNHR)(dppe)$_2$]$^+$. There is a good deal of variation in shift among hydrazido(2-) species and there is a large change from $WF(NNH)(dppe)_2$ ($\delta = 9.6$, the only diazenide value known[36]) to most hydrazido(2-) complexes. But with the limited data at hand it is impossible to determine what exactly is responsible for such variations, whether the effect is principally due to changes in bonding or in magnetic effects.

Applied to hydrazido complexes 1, for which the chemical shift for each NH is above δ 12.2 and $^{1}J(^{15}NH)$ equals 84 Hz, the correlation above suggests that both nitrogens should be planar and involved in π-bonding. The indication of planarity at N(1) from the NMR is in agreement with other results. The x-ray structure shows appreciable multiple bonding of N(1) both with the metal and to a lesser extent N(2). And the infrared offers no contradiction since the NH stretch at metal bound nitrogens does not take on salt-like character (shift to lower frequency, see Table II-8).

Planarity at N(2) is hard to rationalize with the x-ray structure since N(1)-N(2)-C(38) is only 113° and H(35) is sited 25 pm out of this chelate plane (Table II-5). The extent of delocalization of the N(2)-H lone pair of structure 1''' required to give the observed chemical shifts is not at all clear. The modest amount of delocalization in 1,2-diphenylhydrazine is sufficient to give NH resonances as high as δ 7.4. This corresponds to participation of 1'''' in the bonding. (See next page.)



Some contribution of 1" is also expected, but a fairly slight contribution may be all that is required for the observed NMR low field shift. A large contribution of 1" or 1"" would not be consistent with the infrared since ν(NH) of 1 is at higher frequency than is typical of imine and diazene salts.

The PMR data on the hydrazide complexes 1 is not inconsistent with structure 1''' but does accent the necessity of including contributions from 1" and 1"" in any complete picture of the bonding in this compound.

A generally unsatisfactory attempt to record ^{31}P NMR on 1b was made at ambient temperature. The problem was difficulty in keeping the spectrometer frequency-locked. The spectrum had one sharp peak. This implies that the phosphines are equivalent in solution, probably due to rapid interchange (fluxional behavior) via a trigonal bipyramidal iridium complex. Because the solubility of the ionic hydrazido complex was not good at room temperature and was expected to decrease at lower temperatures, no attempt was made to slow this presumed intramolecular exchange to allow observation of two sets of phosphine resonances.

F. Visible Spectroscopy

The red color of the hydrazido complexes **1** is due to a strong absorption of visible light of wavelength near 500 nm (Table II-10). The intensity suggests that it is almost certainly a π->π^* allowed transition of the metal-hydrazido system. Since the energy shows no simple variation with π-donor or acceptor properties of the aryl substituent, it is not possible to make any superficial correlations.

The weaker bands at this same energy in six-coordinate, orthometalated, iridium (III) aryldiazo complexes were assigned to n ->π^* or "charge transfer transition within the metallocyclic ring."[121] A similar hedge against specific assignment was made involving the visible spectra of the tetrazenes **4**.[148]

Table II-10. Visible Absorption (wavelength in nm) of
$[Ir(NHNHC_6H_3R)(CO)(PPh_3)_2]BF_4$ in Methanol

Substituent	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ
1b 2-NO_2(+HBF_4)	515		367			
1b 2-NO_2	532	3.9	ca. 350	3.8	268	4.3
1d 2-F	478		325			
1f 2-OCH_3	495	4.3	ca. 345	3.8		

Chapter III

Synthetic and Reaction Chemistry of $[Ir(NHNHC_6H_3G\text{-}C^6,N^1)(CO)(PPh_3)_2]BF_4$.

A. Introduction

There were several references in Chapter II to other products formed during synthesis of the orthometalated arylhydrazido complexes, 1. The low yields of 1, even after some attempt at optimising their synthesis, are a distinct indication that there is more to the reaction than what was said in Chapter II. The separation of several by-products from at least one reaction has allowed their characterization, which in turn has led us to try modifications to improve the synthesis. Our attempts to increase the yield of 1 have been only partially successful. Even so, the reaction has been so thoroughly studied that it is unlikely that any principal reaction products have gone undetected.

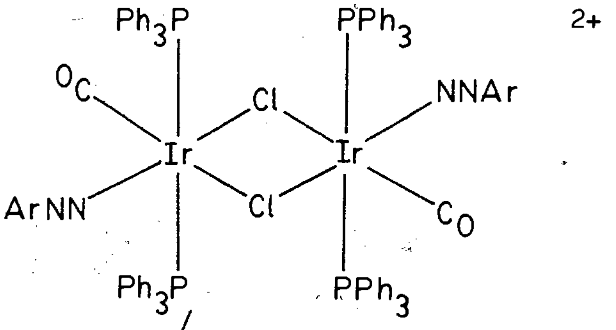
Some of the compounds isolated as by-products of synthetic reactions are probably the result of further chemical reactions on a fully-formed arylhydrazido complex. Since the synthesis and some further reactions of 1 occur together, the two will be discussed together in this chapter. We shall first present results and discussion of genuine reaction by-products, not derived from 1. Then some chemistry of arylhydrazido complexes is presented and discussed. A consideration of the step-by-step mechanism of the orthometalation is given before the experimental section.

B. Results and Discussion

1. By-products Peculiar to $IrCl(CO)(PPh_3)_2$ Reactions

The synthesis of orthometalated arylhydrazido complex **1b** from $IrCl(CO)(PPh_3)_2$ also produced a large quantity of the aryldiazenido complex $IrCl_2(NNC_6H_4\text{-}2\text{-}NO_2)(CO)(PPh_3)_2$, **6**. These two products are thought to be formed in equimolar quantity by this reaction.[94]

$$2\ IrCl(CO)(PPh_3)_2 + 2\ ArN_2^+$$



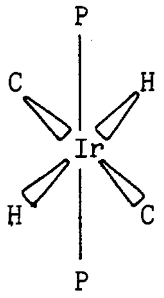
$$\Big\downarrow\ {+}\ C_2H_5OH\ /\ -(CH_3CHO + H^+)$$

$$\mathbf{1b} \longleftarrow Ir(CO)H(NNAr)(PPh_3)_2^+ + IrCl_2(CO)(NNAr)(PPh_3)_2$$

This type of aryldiazenido complex had been previously characterized.[49] No other products were separated in our study.

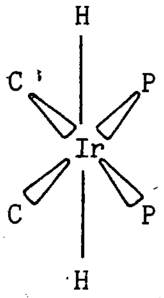
2. By-products Peculiar to $IrH(CO)_2(PPh_3)_2$ Reactions

Reactions of $IrH(CO)_2(PPh_3)_2$, **2**, with benzenediazonium tetrafluoroborates in toluene/propanone were fairly clean. The first material to solidify from crude product mixtures was a white solid analyzing for $[IrH_2(CO)_2(PPh_3)_2]BF_4$, **7**. A material of this composition had previously been identified,[149-151] but the reported infrared spectra do not agree with those of **7** (See Table III-1.) and so a different stereochemistry is suggested. Possible geometric isomers are:



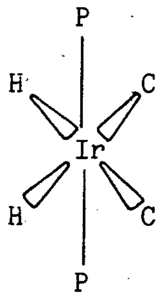
A

all-trans



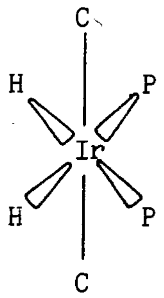
B

H-trans



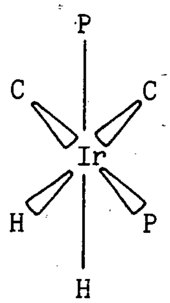
C

P-trans



D

C-trans



E

all-cis

Trans H-Ir-H would show[152] an Ir-H stretch in the range 1615 to 1750 cm^{-1}, which is distinctly lower than the absorptions of 7, and a region in which 7 is transparent. Furthermore the very facile elimination of H_2 suggests that the H atoms are cis. So A and B can be eliminated. Isomer C is that already known.[150] The symmetry of structure D, if it were rectangular at the metal, would be C_{2v}. A reasonable distortion consisting of a shift of the carbonyls and phosphines toward the hydrides could be accomplished without destroying this symmetry. There would be an A_1 and B stretch expected for each of the dipoles Ir-H and C=O. But the A_1 symmetric stretch of nearly trans carbonyls might well have low intensity. And it is empirically known that complexes of cis-dihydrides almost always show only one infrared absorption if they are trans to equivalent ligands.[152] The resultant spectrum of two strong absorptions and one weak accords well with the measured spectrum, given in Table III-1. Since the low-symmetry, all-cis structure E affords no similar, rational explanation for the number and intensity of absorptions, 7 is deemed to have structure D.

Table III-1. Assignment of Infrared Absorptions of **7** in the Metal-Hydride and Carbonyl Region.

Frequency (cm^{-1})		Intensity	Assignment
KBr	Nujol		
2074	2071	wm	νCO A_1
2018	2021	vs	νIrH
2003	1999	vvs	νCO B

Table III-2. Assignment of Infrared Absorptions of **8** in the Metal-Hydride and Carbonyl Region.

Frequency (cm^{-1})	Intensity	Assignment
ca. 2150	m sh	ν(IrH + CO)
2105	s	νIrH trans to P
2005	s	ν(CO + IrH)

The infrared assignments are made in Table III-1. These fall toward the low end of their respective ranges[153], and are lower than the frequencies of comparable vibrations in the isomer of structure C. The possibility of structural confirmation by NMR spectroscopy was lost when a solution of the complex decomposed upon contact with an infrared salt cell.

Small amounts of the isomer of structure C have been detected in some samples of 7 (e.g. see Section III D 3 o). Since the complex of structure C is formed by simple protonation in ethanol[149,150] of the mixture of the two isomers of 2 present in solution (Both are trigonal bipyramidal with axial hydrogen; one has axial carbonyl and the other axial phosphine.[154]), 7 is probably formed indirectly, perhaps by decomposition of an intermediate. (See further below.)

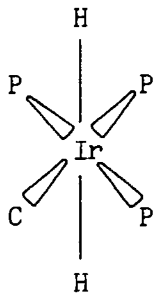
Because less diazonium salt was required, syntheses of 1 from 2 were generally cleaner than from $IrH(CO)(PPh_3)_3$. But the practical difficulty of separating 7 from 1 tended to discourage the use of 2. An optimum strategy might be to use 2, collecting 1 in cases for which 7 could be completely removed before crystallization of 1, and neutralizing reaction mixtures from which 1 and 7 cocrystallize. This was in fact applied to syntheses using $[4\text{-}FC_6H_4N^{15}N]BF_4$.

3. By-products Peculiar to $IrH(CO)(PPh_3)_3$ Reactions

$IrH(CO)(PPh_3)_3$, 3, was similarly protonated during reactions, but the product, $[IrH_2(CO)(PPh_3)_3]BF_4$, 8, did not solidify at all easily and so did not interfere with isolation of the hydrazido complexes 1. It was generally purified by neutralization to recover the neutral iridium hydride 3, but crystallization of solvated 8 from evaporating propanone/water was done once.

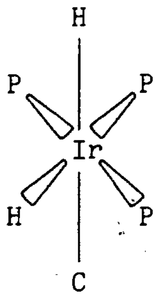
The infrared of 8 is quite characteristic, with peaks of nearly equal intensity at 2005 and 2105 cm^{-1}. A shoulder near 2150 cm^{-1} was never well resolved in solid state spectra. Possible geometries are:

A



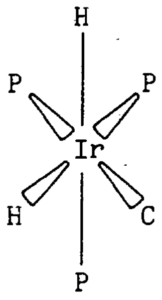
H trans to H

B



H trans to C

C



H trans to P

The lack of low frequency bands eliminates the trans H-Ir-H isomer A and the presence of three bands argues against the facial isomer C since only one hydride band would be expected (on the empirical basis mentioned above). This leaves only the meridional isomer B. Assignment of the infrared bands[155] is made in Table III-2. The complex cation had been previously reported.[149,155,156] A crystal structure of the fluorosilicate salt revealed the meridional isomer B for the cation.[157]

From our results it is not possible to define the route by which the cationic dihydrides are formed. A couple of points do suggest that the reaction is not simply protonation of the neutral molecules, but decomposition of some intermediate: 1) The dihydrides are produced in far greater quantity when the hydrazide is not formed (because of blocking of orthometalation or in dimethylformamide). 2) The geometrical structure of 7 is not that previously formed by simple protonation (Structure C). On the other hand, more dihydride 8 is formed if a reaction is carried out by adding the diazonium salt to a solution containing all the hydride 3, than with the addition of solutions of 3 and diazonium salt together. This suggests that free hydride is simply protonated by the acidic reaction mixture. It was to reduce the possibility of this protonation that simultaneous addition was usually employed.

The same by-product, 8, was produced in larger amounts with two variations from normal synthetic procedures (described below, Section D). When HBF_4 was added to a reaction mixture during combination, 8 was produced in large amount and no arylhydrazido complex 1 was formed. When the addition of $2\text{-}CF_3C_6H_4NNBF_4$ to 3 was done in the presence of LiCl,[158] the only products with a metal carbonyl stretching vibration were $IrCl_2H(CO)(PPh_3)_2$, $IrCl(CO)(PPh_3)_2$ and $[IrH_2(CO)(PPh_3)_3]BF_4$, identified by comparison with the infrared spectra of known samples.

Another by-product largely peculiar to reactions of **3** was an iridium-free material formed from the molecule of triphenylphosphine lost from the iridium in products other than **8**. An obvious possibility was that it reacted in some way with the second mole of diazonium salt. None of the crude products of any iridium hydride reaction showed any evidence of containing excess diazonium salt, though the mole ratio of diazonium to hydride ranged up to three. Clearly then the diazonium ions must be involved in side reactions, but these need not necessarily include reaction with phosphine.

The reaction of triphenylphosphine with diazonium salts has been previously investigated.[159,160] While $[Ph_3PAr]BF_4$ can be formed in over 50% yield, the reaction was found to be strongly affected by change of solvent, acidity, buffer, and aryl substitution. In alcohol the reactions seem to occur via unstable, red diazophosphines, $[ArNNPPh_3]BF_4$. Resonance stabilization involving π-electron donation from a para substituent affords isolable compounds $[Ph_3PNNC_6H_4\text{-}4\text{-}NEt_2]BF_4$ and $[Ph_3PNNC_6H_4\text{-}4\text{-}OMe]BF_4$ in propanone.[93] Otherwise the diazophosphines can either be hydrolyzed to ArH, N_2, and $OPPh_3$[159] or reduced to hydrazo derivatives by excess phosphine.[160] Production of ArH in our reactions was indicated by the distinct mass defect between total reactants and crude, involatile product, more than can be accounted for by loss of N_2, and by the detection of the odor of nitrobenzene from the nitro-substituted diazonium salts.

To complete the picture of this aspect of the reactions, considerable effort was made toward identifying this non-volatile iridium-free product, without success. Rather than displaying particular solubility characteristics, the material just tended to collect with and contaminate crude isolates of other products. However in one reaction of 4-fluorobenzenediazonium salt a small amount of free solid formed in suspension during solvent removal. This was filtered out before it became trapped in later-formed oil, and recrystallized. The product contained no nitrogen and was not $[FC_6H_4PPh_3]BF_4$. Such a formulation does not fit the C,H,N analysis, which does not in fact agree with any acceptable single formulation. More to the point it does not fit the infrared spectrum, which has no aryl-F vibration (ca. 1230 cm^{-1}), 1,4-disubstituted aryl bending absorptions (830 cm^{-1}), or BF_4 stretch (1050 cm^{-1}). The very strong absorptions it does have are common in crude isolates from other syntheses of 1 from 3, so the sample is typical. In general, these strong bands are those expected for Ph_3PBF_3, or a similar compound such as Ph_3PF_2. The band which is not explicable by comparison to literature reports of such four- and five-coordinate phosphorus compounds[161] is the very strong band at 833 cm^{-1}, reported at only medium intensity for Ph_3PBF_3.[162]

If this product of triphenylphosphine reaction is not a quaternary phosphonium salt, which seems to be the case since this would have crystallized out rather easily (MP $[Ph_4P]BF_4$ is 628 K), then there is no tidy explanation for a required stoichiometry of more moles diazonium salt than iridium. The diazonium is however consumed, and with only one mole present, there is probably so little hydrazido complex formed that it can not be isolated.

4. By-product Complexes Formed From Two NNAr Units.

The tetrazene complexes **4** were introduced back in Chapter II because of their structural similarity to the hydrazido complexes **1**. A series of these tetrazenes was isolated and studied extensively by Dr. Alan B. Gilchrist, who obtained them from $IrCl(CO)(PPh_3)_2$ in reactions with diazonium salts in benzene/alcohol solvent mixtures. In addition to the diphenyltetrazene, $[Ir(CO)\{N_4(C_6H_4\text{-}4\text{-}G)_2\}(PPh_3)_2]BF_4$ (G = halide, trifluoromethyl, and methoxy) were reported.[148]

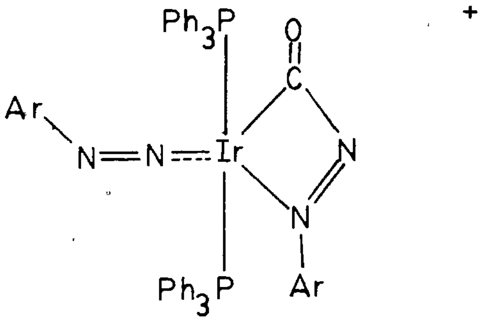
Since this set of tetrazenes was the only one formed from a diazonium salt, it was of considerable interest to define the mechanism of their formation. This has recently been done.[94] Since there is nothing in this mechanism that obviously restricts the formation of tetrazenes with ortho- and meta-substituted aryl rings, it would appear that the principal reason for isolating **4** only with para substituents is that complexes with other patterns of substitution have a far lower tendency to crystallize. They are simply not separated, even though they may be formed in yields equivalent to the yields reported for the symmetric ligands.

In our study of the reactions done to synthesize 1, tetrazenes have been isolated several times from $IrH(CO)(PPh_3)_3$ and once from $IrH(CO)_2(PPh_3)_2$. In the latter case the reaction was done in propanone at low temperature with the reactants not completely dissolved. It is likely that the diazonium salt was in excess in solution, allowing tetrazene formation even though the diazonium:iridium ratio employed was 1:1. The range of tetrazenes was extended slightly but significantly with isolation of bis(4-methylphenyl) and especially bis(2-fluorophenyl) tetrazenes. The latter in particular shows that ortho substitution does not block the formation of other tetrazenes, and that they are simply not crystallizing from crude mixture.

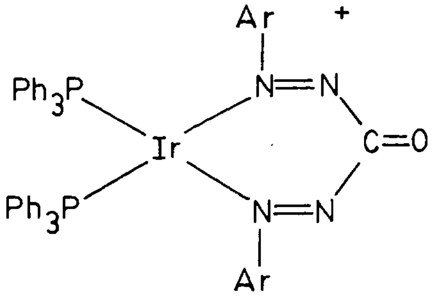
Since the spectroscopic characterization of tetrazenes is not easily done, it should be noted that all those we have prepared absorb strongly near 1500 cm^{-1}. This is possibly a useful group frequency, though it was earlier found not to shift with ^{15}N-substitution.[148]

Neutralization with methanolic KOH of a crude product mixture obtained during synthesis of 1k from 3 produced a neutral complex with a strong infrared absorption at 1497 cm^{-1}. (See Section D 3 b for full spectrum and analysis.) This band was the key to formulation as a tetrazene complex: $Ir(CO_2Me)\{N_4(C_6H_4\text{-}4\text{-}F)_2\}(PPh_3)_2$. Such a substance could be formed by attack of OMe^- at the carbonyl of 4.[163]

Two examples of another complex containing two N_2Ar units have been isolated in small amounts from 2-bromo- and 2-trifluoromethyl-benzenediazonium salts. The complexes 9 precipitated easily from crude reaction mixtures in methanolic HBF_4. These analyzed (See Sections D 3 h and D 3 m.) as isomers of tetrazene 4 or possibly $[Ir\{N_4(Ar)_2\}(PPh_3)_2]BF_4$. They are yellow-green. Their infrared spectra had a strong band near 1675 cm^{-1}, no metal carbonyl absorption, and δ CH patterns (900-600 cm^{-1}) which suggested no orthometalation. They did not form when a complex 1 was reacted with an aryldiazonium salt. Two possible structures for 9 are:



and



5. Products of Oxidation of 1 - Iridium(III) Diazenes 5

As noted at the beginning of Chapter II, my first work with the arylhydrazido complexes involved investigation of chemical reactivity of 1b. This 2-nitro derivative is the least susceptible to aerial oxidation, the most obvious chemical property of 1. It is possible to prepare solutions of 1b in air without obvious immediate oxidation. All other 1 go yellow as quickly as oxygen dissolves in the solutions.

Table III-3. Elemental Analyses of Nitrogen-Containing Iridium Complexes: $[Ir(CO)\{N_4(C_6H_4G)_2\}(PPh_3)_2]BF_4$, **4**; and $[Ir(CO)(N_2C_6H_4G)_2(PPh_3)_2]BF_4$, **9**.

No.	R	Percent Composition					
		Found			Calculated		
		C	H	N	C	H	N
4a	H	56.2	3.94	5.24	56.5	3.87	5.38
4b	2-F	52.4	3.59	4.61	54.5	3.95	4.99
4c	4-F	56.7	3.67	5.08	54.6	3.55	5.20
4d	$4-CH_3$	57.2	4.26	5.08	57.2	4.14	5.24
4e	$4-OCH_3$	55.6	4.11	4.90	55.6	4.02	5.08
9a	$2-CF_3$	52.6	3.36	4.83	52.0	3.25	4.76
9b	2-Br	48.8	3.28	4.71	49.1	3.19	4.67

The oxidation products were orthometalated iridium (III) aryldiazenes, 5, [$AIr(NHNC_6H_3R)(CO)(PPh_3)_2]BF_4$. (See Table III-3. Symbols such as "5a-F" specify the aryl substitution with the lower case letter and A with its chemical symbol, here F.) Aerial oxidation produced complexes with A = F or FBF_3. These were generally produced from unisolated 1 in reaction mixtures, which contained excess BF_4^- and F^-. Halogen oxidation produces complexes with A = Cl, Br, or I. Aryldiazene complexes of the same structure had been isolated earlier from $IrA(CO)(PPh_3)_2$. A variety were identified with A = Cl and single examples were prepared with A = F, Br, I, and $OClO_3$. Since this work had included full spectroscopic[60] and structural[164] characterization, our aim was solely to identify the products of aerial oxidation of arylhydrazido complexes. This was not as straightforward as it might have been because:

1) The expected NH stretching absorption was occasionally absent in spectra prepared by Dr. Farrell, and a peak above 3500 cm^{-1} appeared,[165] so there was some doubt whether we were dealing with one type of complex or two. This problem was resolved: (i) by solution of a crystal structure of a sample of 5b, which had the high frequency infrared absorption by Drs. Sutton and Einstein and Peter Vogel,[97] (ii) by our inability to chemically reproduce the aberrant spectra by variation of synthetic conditions (e.g. the addition of water to reaction mixtures), and (iii) by the mimicing of the spectral features by different preparation of the KBr pellet, with more exposure to water.

2) Recrystallized samples of complexes 5 were not easily identified by analysis since there were three sources of variation: (i) the carbon analyses occasionally were highly inconsistent due to incomplete combustion, (ii) the complexes often crystallized with molecules of solvent, and (iii) the complexes often crystallized as a mixture of both A = F and FBF_3. Substantiation of the last source of variation was offered by isolation and fluorine analysis of pure unsolvated samples of both 5d-F and 5d-FBF_3 from the same reaction. For the FBF_3 complex νCO was about 40 cm^{-1} higher than for A = F. This was the only useful spectroscopic difference between these. It was impossible to detect two different types of BF_4^- as was done[60] with the analogous ClO_4^- complex. The presence of solvent in crystals was verified by PMR of their solutions, but the quantity of pure solid available did not in general allow precise integration. Therefore theoretical analyses of Table III-3 have been calculated without solvent.

That the formation of diazenes 5 from 1 is an oxidation is clear from the equation of the halogen reaction:

$$[Ir(NHNHC_6H_3R)(CO)(PPh_3)_2]BF_4 + X_2 \longrightarrow [XIr(NHNC_6H_3R)(CO)(PPh_3)_2]BF_4 + HX$$

In the products both halogen atoms have become formally X^-, thereby oxidizing the complex 1 by two electrons. The added ligand X^- does not simply occupy the 'vacant octahedral' coordination site of 1. The complex rearranges to give trans phosphines and X trans to aryl in 5.

Table III-4. Elemental Analyses of Nitrogen-Containing Iridium Complexes: $[Ir(A)(NHNC_6H_3G)(CO)(PPh_3)_2]BF_4$, **5**; and $[Ir(NHNC_6H_3G)(CO)(PPh_3)_2]$, **10**.

No.	G	Percent Composition							
		Found				Calculated			
		C	H	N	F	C	H	N	F
5a-F	2-NO_2	49.6	3.93	3.88	8.77	51.6	3.42	4.20	9.49
						50.8	3.98	3.95	8.90[a]
5b-F	2-CF_3	51.1	4.11	2.44	13.7	50.8	3.89	2.58	14.0
5c-F	2-Br	48.1	3.54	2.57		49.9	3.31	2.71	
5d-F	4-F	52.9	3.55	2.94	11.6	53.0	3.52	2.88	11.7
5d-FBF_3	4-F	49.6	3.52	2.57	16.1	49.6	3.29	2.69	16.4
5e-F	4-CH_3	54.7	4.10	2.82		54.5	3.85	2.89	
5f-F	4-OCH_3	51.9	3.72	2.62		53.6	3.78	2.86	
10a	2-NO_2	59.4	4.14	3.95		57.7	3.83	4.70	
10b	2-CF_3	57.7	4.14	2.80		57.6	3.75	3.05	
10c	3-NO_2	52.4	3.88	4.63		57.7	3.83	4.70	
10d	4-F	59.2	4.10	3.18[b]		59.5	3.95	3.23	

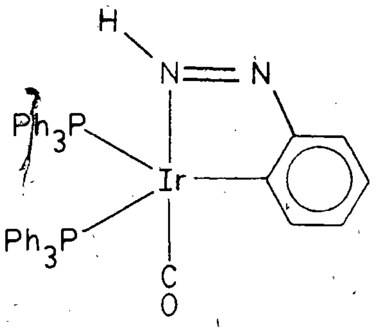
a) Calculated including 2 CH_3OH.

b) Average of two trials: C using V_2O_5 was 59.8%, without V_2O_5 58.5%.

Since rearrangement of an isomer of 5 with different geometry about the metal, via a dissociative mechanism, is entirely possible, the final stereochemistry can not be used to imply anything about the site of oxidation - metal or diazo ligand.

6. Product of Neutralization of 1 - Iridium(I) Diazenes 10

The arylhydrazido complexes 1 were mildly acidic and were deprotonated by Et_3N, hydroxide, or carbonate but not hydrogen carbonate. The product was an iridium (I) aryldiazene 10.



10

Most of these were red; the 2-nitroaryl derivative was purple. They were most easily obtained as pure solids by chromatography followed by trituration with ether, in which they were only slightly soluble. (See further Section D 4.) They were soluble in all common solvents except water and hexane and could not be selectively precipitated from solution.

The problem with the purification and identification of 10 stemmed from the existence of a substance, which we call the "pseudodiazene", with closely comparable infrared spectrum and color (The 2-nitroaryl derivative was blue; others were maroon.) which eluted with 10 when a silica gel column was developed with mixed solvents, e.g. benzene/ether. To increase the opportunity for full separation of mixtures during chromatography, a rather long column seemed preferable. With polar solvents the separation was not good, so benzene or toluene were used. But with neat aromatics complex **10** moved too slowly to be practical with long columns so small percentages of ether were added. Because this allowed development of a single band we did not quickly appreciate that the eluate was a mixture. The aryldiazene **10** is effectively separated on a short (5-10 cm) silica gel column using neat aromatic solvent.

The pseudodiazene was produced with an excess of anionic base. It was never solidified, and dissolved well in all solvents except hexane and water. It did not move ($R_f < 0.1$) on silica gel with neat benzene or toluene, but did with addition of small amounts of polar solvent. The infrared of this by-product had νCO shifted down to 1940 cm^{-1} and stronger (i.e. medium) intensities near 720 and 540 cm^{-1} compared to values found for **10** with the same aryl substitution. An NH-stretching absorption was unobserved or very slight (probably due to small amounts of **10** present). On the basis of these properties one might have suggested formulation as $[Ir(NNC_6H_3G)(CO)(PPh_3)_2]^-$, but the C, H and N analyses were all low for this or any similar product (see below, Section D 3 1). The nature of the pseudodiazene remains unknown.

The existence of the remaining NH in **10** was shown by a very weak infrared band near 3285 cm^{-1}. Its position at N(1) was ascertained by PMR of the ^{15}N(1) isotopically substituted complex, which showed a sharp doublet at δ 12.0, corresponding to one NH split by coupling to the nitrogen, with $J_{(^{15}NH)}$ = 81 Hz. Characterization of the metal as iridium(I) was allowed by the carbonyl stretching frequency of 1955 cm^{-1}. With a d^8 metal the iridium(I) complex is expected to be trigonal-bipyramidal rather than square-based pyramidal as 1, though the actual geometry of 10 is probably highly distorted from the ideal. The small bite of the orthometalated aryldiazene could not be accommodated in the trigonal plane, so either the N or aryl must be axial. On the grounds of putting the carbonyl trans to the diazene where it is frequently located, perhaps because of favorable interaction through the metal with the π-system of the diazene, we assign the geometry diagrammed above to complexes 10.

The neutral aryldiazene complexes 10 can be reprotonated to 1. The difference in carbonyl stretching frequency between the arylhydrazido complex 1 and the iridium(I) aryldiazene 10 implies that this reversible deprotonation/protonation involves appreciable electron shift to or from the metal. A mere change in charge on the complex would account for only 10 cm^{-1} of this difference.[166] But the shift of electron density from the metal in the protonation of 10 to 1 is of a different sort than that in the oxidation of 1 to 5. To help show this and to clarify the web of interrelations between the several known orthometalated iridium aryldiazo species, Figure III-1 is given. It pictures a number of possible reactions simultaneously as passages between vertices of a trigonal prism. The upper face of the prism is a

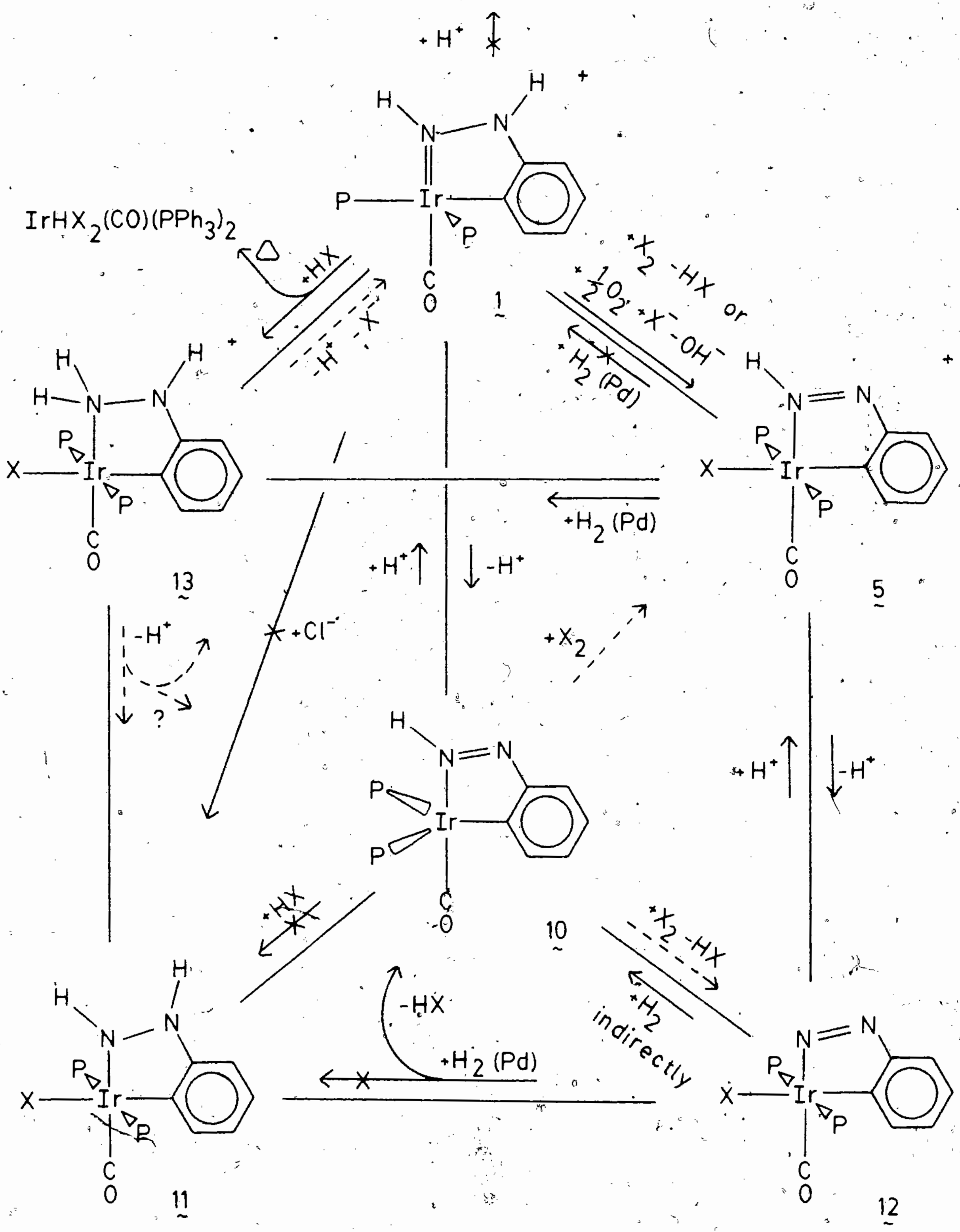


Figure III-1. Reactions of Orthometalated Aryldiazo Complexes of Iridium

Reactions indicated as dashed arrows have not been done definitively.

Reactions indicated with crossed arrows do not occur at the conditions used.

set of known cationic species; on the lower face are neutral complexes related by loss of a hydrogen ion. The neutral complex 11 in the lower left corner is unknown and probably non-existant, as will be discussed. Those on the right edge (5 and 12) are more oxidized than the others. Reactions to form these from the other species would be an oxidation, e.g. the reaction of 1 to 5, discussed in Section 5 just above, which can be seen as an oxidative addition of X_2 to a coordinatively saturated d^8-metal complex.

Transformations between 10 and 11 or 13 involve change of oxidation state of the metal, but by a shift of electron density between the metal and the diazo ligand. They are not oxidations of the complex and so are not oxidative additions.[167,168] The relation between 10 and 1 is of the same sort. In their similar transfer of electron density to the ligand on protonation, reactions such as[169]

$$RhCl_2(NNAr)(PPh_3)_2 \underset{+Et_3N}{\overset{+HCl}{\rightleftarrows}} RhCl_3(NHNAr)(PPh_3)_2$$

resemble this aryldiazene-arylhydrazido system.

7. Other Reactions Related to Figure III-1.

Addition of LiCl to a methanolic solution of 1b had no effect on its visible spectrum. Addition of LiCl to a methanolic solution of 1a followed by precipitation with water and drying under vacuum left a mixture which appeared by infrared to contain $[Ir(NHNHC_6H_4)(CO)(PPh_3)_2]Cl$ from anion exchange and $[Ir(NHNC_6H_4)(CO)(PPh_3)_2]$ from loss of volatile HCl from the chloride salt. Since no Ir-Cl stretch was seen near 300 cm^{-1}, there was probably no $IrCl(NHNHC_6H_4)(CO)(PPh_3)_2$, 11, present in the product. So in the arylhydrazido complexes 1 there would seem to be enough donation of electrons from N(1) that the iridium is coordinatively saturated (Recall resonance form 1''' in Chapter II.). Support for the lack of coordination came from the reaction of tetrazene 4 with LiCl, which also gave apparently simple anion exchange because there was no change of color and little shift in carbonyl stretching frequency. Complex 11 does not form from 1; it is probably unstable in solution with respect to either 1 or 10 depending on solution acidity.

This instability of 11 was obvious in earlier work as well. When palladium-catalyzed H_2-reduction of one example of 12, $[Ir(NNC_6H_3\text{-}4\text{-}Br)(CO)(PPh_3)_2]$, was accomplished, the product obtained was not the expected[170] 11 but 10.[60] We feel the hydrogen reduction required catalysis because it occurred at the diazenide rather than at the metal, that the immediate reduction product was indeed 11, but this simply lost HCl to the solution, leaving 10.

The remaining reactions of 1 are those with acid. The arylhydrazido complexes 1 are not visibly changed by an excess of HBF_4 and do not appear to be further protonated under normal solution conditions. It is not surprising that the iridium(I) aryldiazenes 10 can not be doubly protonated. Most diazenes are not basic enough to be further protonated even once, to hydrazides. This is clearly connected with the fact that most diazene complexes have a six-coordinate d^6 metal configuration, unlikely to be effective at supplying further electron density to a diazo ligand. The one reported d^8 metal diazene is[80] $[PtCl(NHNAr)(PEt_3)_2]BF_4$. No mention has been made of any attempt to react this with HCl, which might produce $[\{PtCl_2(NHNHAr)(PEt_3)_2\}_2](BF_4)_2$ or $PtCl_3(NHNHAr)(PEt_3)_2$.

The process of fixation/reduction of dinitrogen is one of supplying electrons to the diazo ligand. Chapter I emphasized the number of hydrogens (or organosubstituents) because this is the best measure of how effectively metal complexes can move electrons onto the diazo ligand. It is still hard to predict if a given complex has a diazo group sufficiently basic for protonation or at which nitrogen this protonation will occur, as is obvious in the work of Chatt's group on group VI dinitrogen complexes[82] (See Chapter I.), in the reactions[139]

$$ReCl_2(NNPh)(NH_3)(PMe_2Ph)_2 + H^+ \rightarrow ReCl_2(NNHPh)(NH_3)(PMe_2Ph)_2^+$$

$$ReCl_2(NNPh)(PMe_2Ph)_3 + H^+ \rightarrow N.R.,$$

and in the group VI complexes described in the next chapter.

The arylhydrazine complex 13 (Figure III-1) had been prepared by catalytic hydrogenation of diazene 5.[60] It would seem that the addition of HX to 1 might also produce 13, but this did not occur at room temperature with dilute methanolic solutions of HBr or HCl. As with methanolic HBF_4, the hydrazido complex was not protonated; as with X^-, a simple anion exchange occurred. With mild heating (ca. 320 K) methanolic HBr did react with 1, producing $IrBr_2H(CO)(PPh_3)_2$. The decomplexation of orthometalated arylhydrazide did not occur via the orthometalated aryldiazene complex 5 because a similar heating of 5 with HCl or HBr solutions was tried without reaction. Because the uncomplexed aryl product was not isolated, one can not say if the reaction occurred via the arylhydrazine complex 13.

Three trials with very small amounts of impure 2-nitroarylhydrazido complex 1b prepared by Dr. Nicholas Farrell, two with HCl and one with HBr addition, showed similar room temperature inertness of 1, but in each case the solutions were evacuated under vacuum and as they became concentrated near dryness a color change did occur to yellow-brown. By the time these samples were recrystallized they were aryldiazenes 5, analytically difficult to distinguish from arylhydrazines 13, but characterized by infrared spectra. A crude sample was distinctly different however, with infrared absorption as expected for an iridium(III) (ν CO 2060) arylhydrazine (νNH ill-defined 3300, 3240, 3140, δ NH_2 1600 cm) complex 13 with a hydrazine N(2) lone pair in conjugation with the nitro group (ν_{asym} NO_2 1511, ν_{sym} 1340 m, 1300 s) and a chloride trans to the metal-aryl bond (ν IrCl 290 cm^{-1}). Though this evidence for 13 is sketchy, it does appear that the reaction did occur with very concentrated, probably molecular, HX.

Though 13 may not be acidic, we suspect that it would react with base to generate 11 and then 10, the neutral iridium(I) aryldiazene. This tendency to reduce the metal upon deprotonation of a complexed hydrazine is one reason so few hydrazide and hydrazine complexes are known.[77] Syntheses of other hydrazido complexes are as likely to come from diazene chemistry, like 1, as from hydrazine chemistry.

8. $IrH(dppe)_2$ and $RhH(CO)(PPh_3)_3$ Reactions with Diazonium Ions

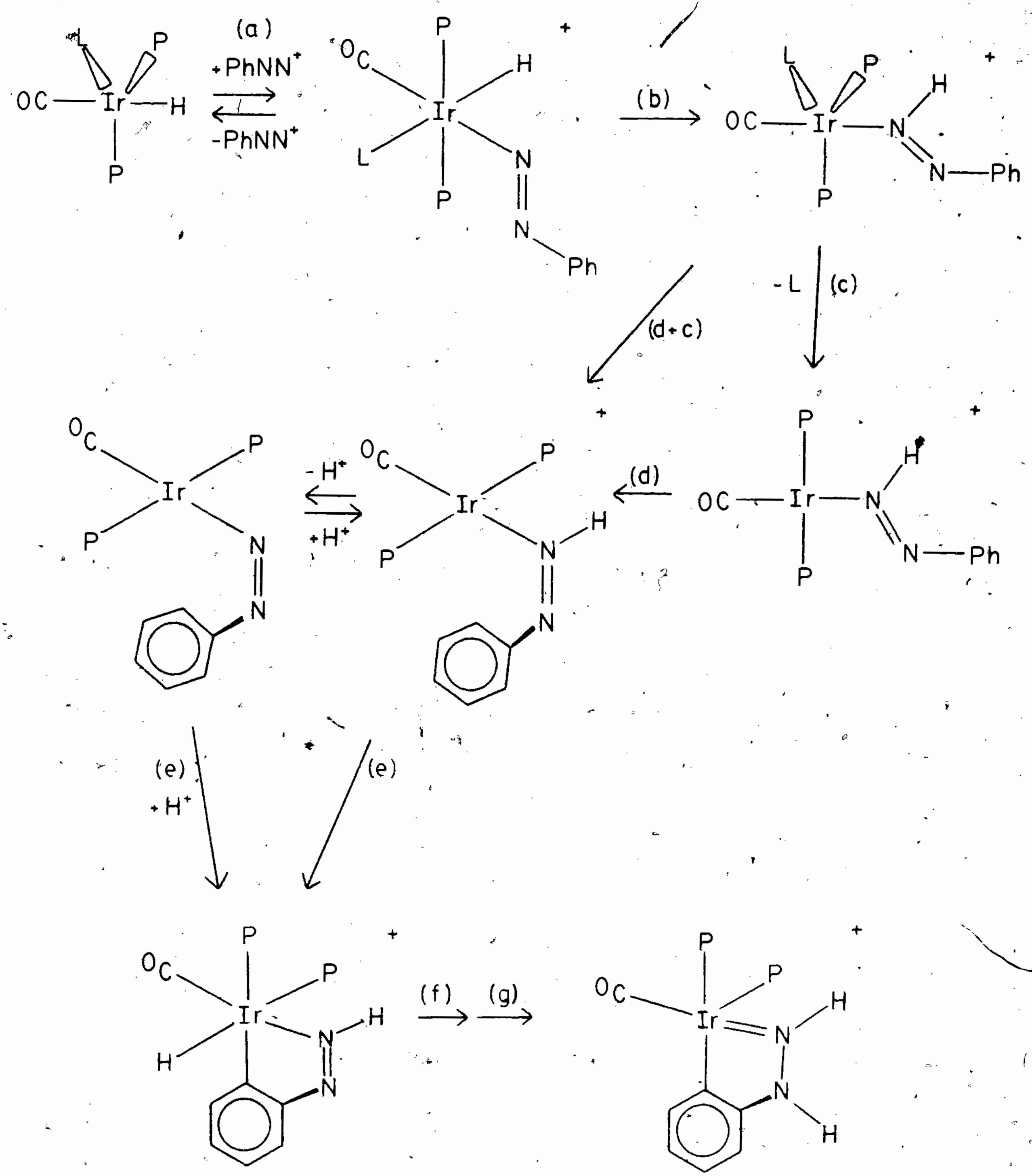
Two further variations of metal complex closely related to $IrH(CO)(PPh_3)_3$ have been reacted with diazonium salts. Under argon $IrH(dppe)_2$ formed $Ir(dppe)_2BF_4$. Since this occurred even at low temperature, the reaction may be one of electron transfer to the diazonium ion and decomposition of the radicals produced. When the reaction was done under an atmosphere of N_2, the involatile, solid isolate absorbed at 2060 cm^{-1}, suggesting the presence of $Ir(N_2)(dppe)_2BF_4$. By comparison with the known $MH(N_2)(dppe)_2^+$ where M is an iron family metal,[170] this iridium complex may be reasonably stable.

Preliminary work with $RhH(CO)(PPh_3)_3$ suggested that it reacted with diazonium salts without loss of N_2 but without orthometalation as well, giving a diazene $[Rh(CO)(NHNPh)(PPh_3)_n]BF_4$. It would be of obvious interest to isolate such a complex and compare its chemistry to that of the other d^8-metal diazenes, 10 and $[PtCl(NHNPh)(PEt_3)_2]BF_4$.

C. Discussion of the Mechanism of Orthometalation.

A good deal of effort has been spent trying to ascertain the mechanism for the formation of the tetrazenes 4 and orthometalated aryldiazenes $[IrCl(CO)(NH{=}NAr)(PPh_3)_2]BF_4$ from the reaction of diazonium salts with Vaska's complex in the presence of alcohols.[94,171] The hydrazido complexes were an integral part of that effort. The established, overall picture is that an iridium(I) complex of aryldiazene or aryldiazenide either is attacked by a further diazonium cation to form tetrazene or is orthometalated.[94] The details of the orthometalation itself would be even more difficult to pin down than was the gross picture. Still, it is useful to discuss the process in terms of a proposed mechanism for orthometalation and to point out the particular features of this example.

A complete mechanism based on a concerted addition step (vide infra) is given in Figure III-2. Step (a) is the coordination of electrophilic ArN_2^+ to the metal, analogous to protonation, creating a six-coordinate Ir(III) complex. In step (b) the aryldiazenido ligand



1

Figure III-2. Mechanism of Formation of $[Ir(NHNHC_6H_4)(CO)(PPh_3)_2]BF_4$.

inserts into the iridium-hydride bond, forming a five-coordinate Ir(I) complex which (c) loses L (the third phosphine of **3** or the second carbonyl of **2**) to become a square-planar complex. The same complex is believed to be formed from $IrX(CO)(PPh_3)_2$ and diazonium salts in alcohols.[94] Phosphine does partially dissociate from **3** in solution[172] but this is not likely to be the first step in the mechanism since: i) this would not parallel the reaction of **2** from which carbon monoxide does not dissociate at room temperature, and ii) this dissociation is far slower[172,173] than formation of **1** at room temperature.

There is no direct evidence which bears on the sequence of the insertion of N(1) into the Ir-H bond and the dissociation of L. The ruthenium and osmium complexes $[MH(NNPh)(CO)(PPh_3)_2L]^+$ readily lose L trans to H.[174] The same reaction could occur for the iridium analogue, but the five-coordinate intermediate from such a dissociation, $[IrH(NNAr)(CO)(PPh_3)_2]^+$, would likely contain singly-bent ArNN with a non-basic N(1).[45] The aryldiazenide in the intermediate corresponds to a carbonyl or linear nitrosyl in qualitative electronic structure. Since these do not insert into a metal-hydride bond, it is unreasonable to postulate that a singly-bent aryldiazenide would either. The indirect evidence thus suggests that the insertion is unlikely to occur if a dissociation occurs first and so argues against reversing the sequence of steps b and c.

Crystal structures of two platinum complexes analogous to our square-planar intermediate, $[PtCl(NHNHAr)(PEt_3)_2]ClO_4$ [175] and $[Pt(CCPh)(NH{=}NAr)(PPh_3)_2]BF_4$,[125] show that the aryldiazene is cis and that the NH=NC plane is perpendicular to the coordination plane, but the energy difference between the cis and trans isomers of coordinated aryldiazene is probably quite small.[176] The aryl ring must be bent toward the metal (the diazene must have trans geometry) for orthometalation of the iridium complex, so conversion to a trans diazene is step (d). A platinum imine complex is known to have this required trans structure.[177]

The critical step (e) is an oxidative addition[167] of C(aryl)-H to the iridium. Vaska's complex, $IrCl(CO)(PPh_3)_2$, is very well known for the oxidative addition reactions it undergoes. It has been determined that the common examples all occur to give cis-added ligands.[178] This is the stereochemistry represented in Figure III-2.

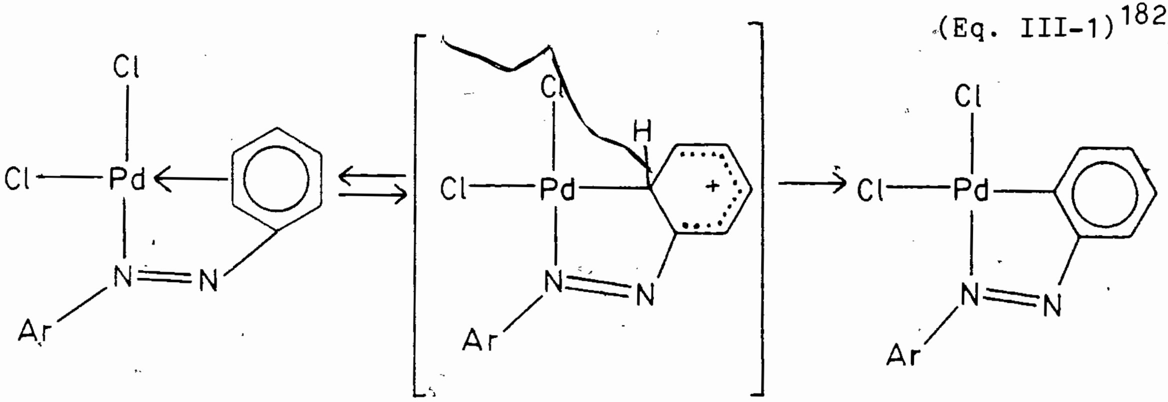
While there is precedent for this orthometalation, its ease is rather surprising. For instance, though the addition of halobenzenes to $[IrCl(CO)(PPh_3)_2]$ has been reported,[179] the rate of this reaction is appreciable only at elevated temperatures (>400 K). And the related azo-iridium complexes $IrCl(ArNNAr)(PR_3)_2$ orthometalated at room temperature, but only slowly.[180] Especially in comparison to the diaryldiazene case, no definite basis for the rate enhancement in our reactions is apparent.

Steps f and g constitute together the shift of a proton from the metal to N(2). It appears that N(2) is a significantly more basic site than the metal. Deprotonation of iridium hydrides is not generally rapid (e.g. 8, See Section D.), but no buildup of Ir(III) hydride during reaction was detected.[158]

Orthometalations have previously been described in terms of three mechanisms. These are: 1) the concerted insertion of a nucleophilic metal into a C-H bond,[181] 2) nucleophilic aromatic substitution, and 3) electrophilic aromatic substitution.[182,183] None has been well investigated.[184] The latter two mechanisms have been modeled on those of typical organic substitutions at an aromatic ring since the organic moiety is commonly an aryl ring, and it has been stated that only these two apply to cyclization of N-donor ligands.[184,185]

The most straightforward model mechanism is that related to a typical S_E aromatic substitution: the metal is attacked by electrons from the aryl ring, preferentially at the site of greatest electron density. The proton at the site of M-C bond formation dissociates and the aromaticity is restored.

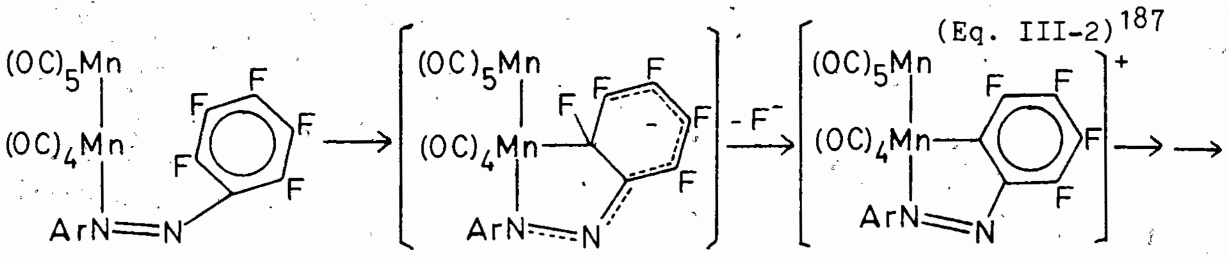
(Eq. III-1)[182]



The metal is electrophilic and does not change its coordination number or formal oxidation state during the reaction. The leaving group is an acid which leaves from the carbon. Since the Ir(I) complex which undergoes metalation in our studies is most unlikely to be appreciably electrophilic, this mechanism does not apply.

Several closely related models are all nucleophilic mechanisms. For substitution of a halogen by a metal atom at an ortho site, a mechanism related to a typical $S_N(Ar)$ reaction[186] can be written.

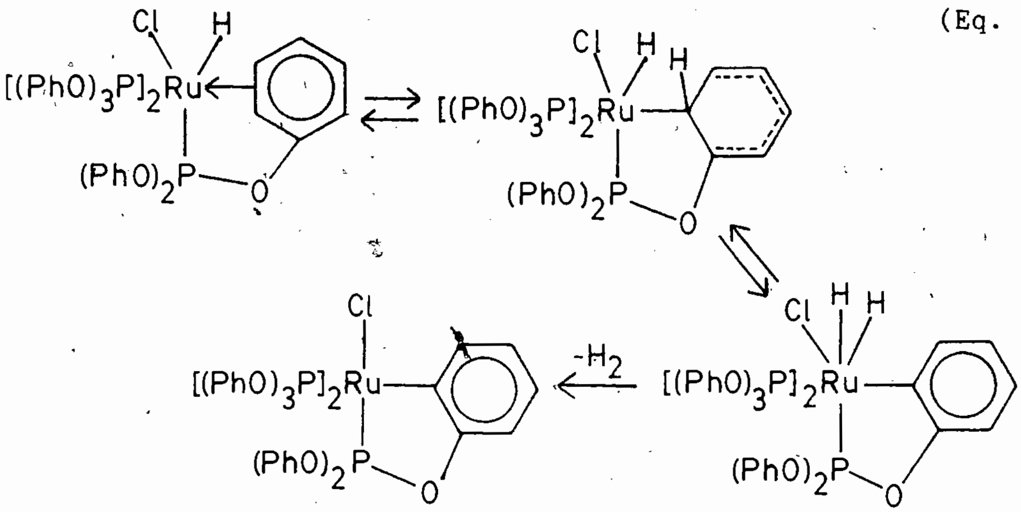
(Eq. III-2)[187]



This is not known for a leaving hydride and can not be satisfactorily applied to our Ir(I) orthometalation, especially since the 2,6-difluorobenzenediazonium salt does not orthometalate.

A detailed mechanism depicted by Parshall[182] is a vitiation of the nucleophilic alternative above.

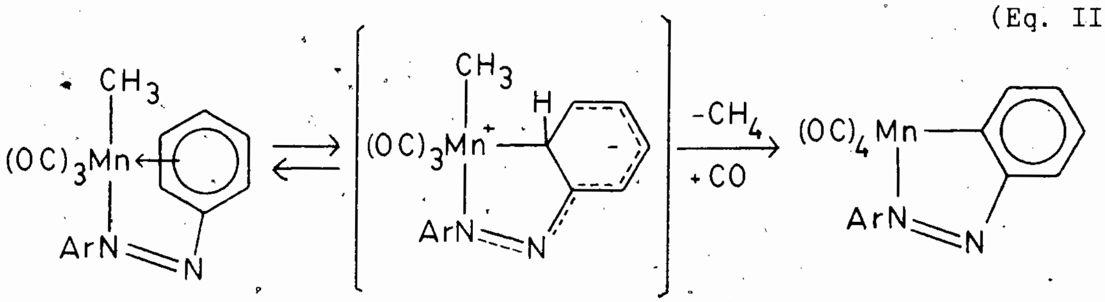
(Eq. III-3)[182]



Because Parshall showed no charges or oxidation states, it is not clear what he means by his drawing but it appears to represent a nucleophilic attack by the metal on the ring followed by a 1,2-hydride shift and elimination of H_2 from the metal.

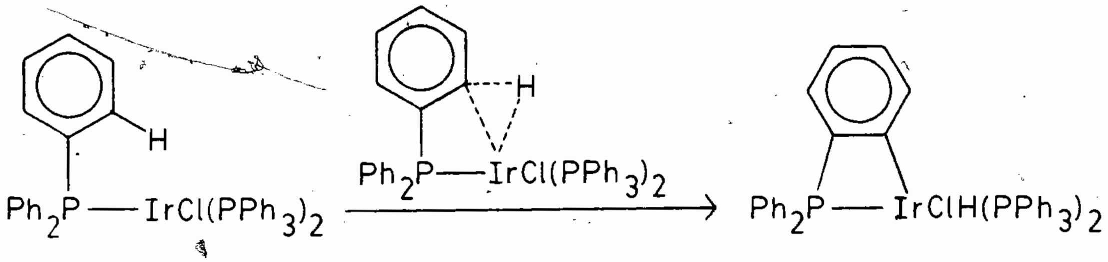
Orthometalation of a d^6-manganese intermediate formed from $MnCH_3(CO)_5$ and 3-fluorophenyl(phenyl)diazene was described as a nucleophilic attack at carbonyl by Bruce,[183] but no delineation was given of this mechanistic pathway. A pathway related to Parshall's can be written.

(Eq. III-4)



While an $S_{N(Ar)}$ mechanism such as these could be applied to our iridium(I) chemistry, the ease of orthometalation found even with electron donating ring substituents discredits the idea. Note however that the product of the two steps of nucleophilic attack and 1,2-hydride shift is the same as that directly obtained by concerted addition[181] of the metal into the C-H bond.

(Eq. III-5)[181]



This is the third mechanism proposed for orthometalation. It is sometimes referred to as the oxidative addition mechanism,[184,185] though this is ambiguous since oxidative additions occur by several mechanisms,[188] including nucleophilic substitution like that just discussed. For Equation III-5, which is clearly related to our diazene orthometalation of Figure III-2, the metal must be electron-rich,[180] but it is not acting as a classic organic nucleophile in that it is attacking at two atoms. The metal is increasing its coordination and oxidation numbers during the reaction (oxidative addition) and in this example the product is stable to loss of HCl (reductive elimination). This mechanism finds its precedent in transition metal chemistry rather than in organic chemistry.

In this scheme the aryl π-system is not directly involved. This agrees well with our observation that changing aryl substituents from a strong π-acceptor (NO_2) to a strong π-donor (OMe) has no marked effect on the apparent rate of reaction.

This concerted addition is clearly the preferable mechanism for our iridium(I) system. Parshall[181] and Dehand[182] stated that orthometalation depends on the ligating atom, N or P; that the concerted processes are characteristic of P-donor ligands. Our work and that of Vrieze[180] would suggest that the ligating atom of the orthometalating moiety is less important than a high metal electron density, commonly found in N-donor complexes as well.

Bruce and Goodall note that metalation of a 3-fluorosubstituted aryldiazo group by nucleophilic attack on the ring should occur to give preferentially a 1,2,3-substituted product, e.g. with attack ortho to both the fluoro and diazo sites, because of the inductive effect of the fluorine.[183] They argued that the observed preference for this stereochemistry in the products from azobenzenes and $CH_3Mn(CO)_5$ proves that the nucleophilic mechanism applies. Our infrared evidence suggested the same stereochemistry with the 3-fluoro derivatives. This can be rationalized with a concerted mechanism as well, considering the effect of a neighboring fluorine on the C-H σ^* energy, the LUMO of the reaction center.[180] It is our opinion that few of the orthometalations of nucleophilic metals go through an intermediate with a pseudotetrahedrally coordinated orthoaryl carbon atom as has been commonly represented.

D. Experimental

1. Instrumentation

Elemental analyses were determined by Mai-Keng Yang of the microanalytical laboratory at Simon Fraser University (C, H, N) and by H. Reuter of the A. Bernhardt Microanalytical Laboratory, Germany (F and a few C, H, N).

Infrared spectra were recorded as dispersions in KBr discs on a Perkin-Elmer 457 grating spectrophotometer using polystyrene to calibrate. KBr discs were prepared in a dry box with a Wilks minipress, which blocked off over half the sample beam. To enlarge the range of % transmittance in such spectra the "100% transmittance" comb was opened and the reference beam attenuated so that percent transmittance at 4000 cm^{-1} was increased to thrice its unattenuated value or 80% of full scale, whichever was less. With this procedure the gain was such that spectra run at medium speed (0.25 h/spectrum) were consistently sharp. While the absorption frequencies of a given pellet were almost always reproducible to ± 3 cm^{-1}, the accuracy was not this good because a) the sensitivity of the instrument was low near 2000 cm^{-1} (Peak positions between 2015 and 2000 cm^{-1} recorded on both the 4000-2000 and 2000-600 cm^{-1} gratings rarely agreed.), b) some peaks seem to shift in a different pellet pressing, and c) there was no calibration below 600 cm^{-1}.

In reporting infrared spectral intensities we have used a scale which appears to be both useful and in agreement with intuition. The scale is based on absorbance, each boundary being 2.25 times greater than the last. Because the mesh of the scale is fine enough, a few spectra recorded on inadvertantly very concentrated or dilute pellets were adjusted by shifting all intensities one unit, to agree with intensities of similar complexes.

Table III-5. Abbreviations Used to Designate IR Intensities

Transmittance (%)		96		91		82		63		36		10		0.6	
Intensity Abbreviation*	vvw		vw		w		wm		m		s		vs		vvs
Absorptivity		.017		.039		.088		.20		.44		1.0		2.25	

* Letters are applied as usual to mean: v, very; w, weak; m, medium; s, strong. Peaks of vvw intensity not reported; peaks of vvs intensity not usually differentiated from vs strong because spectrometer not calibrated sufficiently well.

Proton magnetic resonance spectra were recorded on Varian A-56/60 and XL-100 spectrometers at ambient temperatures (ca. 305 K) unless noted. Positive chemical shifts are reported in parts per million (δ) downfield from $(CH_3)_4Si$.

Raman spectra were obtained with a Cary 81 spectrometer with He-Ne laser excitation from a Spectra-Physics Model 125 laser.

Visible-ultraviolet solution spectra were measured on Unicam SP 8000 or Cary 17 spectrophotometers in quartz cells.

Electrical conductance was determined with a Radiometer Type CDM 2d conductivity meter. The cell used was designed for use with small volumes (>3 ml) solution, and could be drained to, and refilled from, a closed pear-shaped flask, allowing measurement under N_2 atmosphere.

Melting points were obtained for samples heated in air on a Fisher-Johns apparatus.

2. Starting Materials, Solvents and Apparatus.

Variously substituted benzenediazonium tetrafluoroborates were prepared at 273 K according to the method of Roe using HBF_4.[189] Except for the $^{15}N(1)$ analogues, about 35 mmoles of unpurified, commercial aniline derivative was reacted and the sodium nitrite solution added until a positive starch-iodide test was obtained with the reaction solution. Yields paralleled those reported previously.[189] Hexafluorophosphate salts were prepared in the same manner. For the $^{15}N(1)$ diazonium salts analytically pure anilinium tetrafluoroborates were prepared and the $Na^{15}NO_2$ added stoichiometrically by weight. The diazonium salts were stored in the dark at 268 K. If not recrystallized within the previous two months, or if decomposition were evident by color in the sample, the salt was further recrystallized from propanone/ether.

Na_3IrCl_6 was generously loaned by Johnson, Matthey and Co. $IrCl(CO)(PPh_3)_2$,[190] $IrH(CO)_2(PPh_3)_2$,[172] $IrH(CO)(PPh_3)_3$[191] and $IrH(dppe)_2$[192] were synthesized according to literature methods using unpurified commercial samples of the appropriate phosphines. Purity was checked by infrared and analysis. One preparation of $IrH(CO)(PPh_3)_3$ did contain a bit of $IrCl(CO)(PPh_3)_2$, recovered easily as methanol insoluble material after a reaction. $RhH(CO)(PPh_3)_3$ was prepared by Dr. Nicholas Farrell and contained $RhCl(CO)(PPh_3)_2$.

Solvents were reagent grade and distilled under nitrogen before use from generally used strong reducing agents. This was not sufficient for work with the hydrazido complexes because of the small quantities of complex often involved, so much of the work (except for the reactions with HX and X_2) was done with solvents degassed immediately before use by repeatedly evacuating a side-arm tube containing the solvent, and then refilled with N_2. The "methanolic HBF_4" solution commonly used in this work was prepared by adding a few drops of 48% aqueous HBF_4 to methanol to make a concentration of about 0.02 M.

The manipulations described were greatly facilitated by the use of a bench-top vacuum rack with three-way taps allowing connection to either the vacuum line or a N_2 tank. The rack was attached to side arms of reaction vessels with thick-walled Tygon tubing. The glassware was of standard Schlenk-type except that some use was made of filter sticks having frits of Corning medium porosity trimmed to 1 cm diameter. This allowed easier collection of small quantities of product.

3. Reactions of $IrH(CO)L(PPh_3)_2$ with Diazonium Salts

a. Reaction of Iridium Hydride with $C_6H_5N_2^+$.

A three-neck round bottom flask was equipped with two pressure-equalizing addition funnels and a tap to a vacuum/N_2 connection. The funnels were loaded with solid $IrH(CO)(PPh_3)_3$ (301 mg, 0.299 mmole) and benzenediazonium tetrafluoroborate (117 mg, 0.612 mmole) and the entire system evacuated and refilled with nitrogen. Degassed solvents (30 ml toluene and 15 ml propanone) were added to the respective funnels with precautions against contamination by O_2. The hydride and diazonium reagent solutions were added simultaneously to the flask while the mixture was stirred at room temperature, starting with hydride but keeping the flows balanced so that additions of the two reactants ended simultaneously after 0.1 h. The solution went red-orange. It was stirred another 0.2 h and then partially evaporated under vacuum, with no external heating or cooling of the flask. After 1 h, with about 20 ml of deep red solution remaining, this was decanted from the brownish oil which had formed on the walls of the flask. Both oil and decantate were evacuated to complete dryness.

The hydrazido complex 1a was recovered from the decantate as follows. The residue was dissolved in 1 ml methanolic HBF_4, then addition of 3 ml Et_2O and 4 ml hexane gave some oil. Another 0.2 ml methanolic HBF_4 was added to redissolve the oil and the solution was then briefly evacuated while being stirred very vigorously. The orange solid 1a which formed was filtered, washed twice with ether and vacuum dried. (See Table II-1 for analyses of hydrazido complexes 1.) With heating in air, 1a decomposed without melting above 396 K; it decomposed with melting when placed on a hot stage above 428 K. When a Raman spectrum was attempted, the sample decomposed in the beam.

The early-oiling material was treated with 1.6 ml methanolic HBF_4 and the maroon solid tetrazene 4a (61 mg, 20%) which formed was filtered, washed twice with 1.5 ml 1:3 methanol/ether and vacuum dried. (See Table III-3 for analyses of 4.) IR: 3060 wm, 2031 vs (ν CO); 1587 wm, 1576 sh, 1483 s, 1454 w, 1437 s, 1333 w, 1313 wm, 1281 w, 1266 w, 1232 w, 1220 w, 1190 wm, 1163 wm, 1088 vs, 1055 vvs, 1035 sh, 1011 m, 1000 s, 930 wm, 848 w, 744 s, 692 vs, 615 w, 567 m, 534 s, 514 vs, 457 wm, 420 cm^{-1} wm.

3b. Reaction of Iridium Hydride with $4\text{-}FC_6H_4N_2^+$.

Synthesis of 1k was done in the manner of 1a, using a large quantity of hydride 3 (425 mg, 0.422 mmole) and correspondingly larger quantities of diazonium salt and solvents. The early-oiling material was dissolved in 1 ml methanol and tetrazene 4c crystallized as a single large red crystal cluster (51 mg, 11%) by addition of methanol and cooling to 268 K. The crystal turned to powder with vacuum drying. Characteristic IR: 2039 (ν CO); 1499; 1218 (ν arylF); and 837 cm^{-1} (δ CH of 1,4-aryl).

The hydrazido complex 1k solidified from late-oiling material in methanolic HBF$_4$/ether on standing and was filtered and washed with ether. IR: 3283 m, 3056 wm, 2003 vs, 1603 wm, 1589 w, 1564 m, 1509 w, 1482 m, 1465 wm, 1434 s, 1311 wm, 1278 wm, 1244 wm, 1210 sh, 1193 m, 1162 m, 1115 s, 1189 s, 1053 s, 999 m, 888 2m, 864 w, 794 wm, 742 s, 693 s, 658 w, 574 wm, 550 wm, 519 vs, 475 wm, 452 wm, 418 wm, 313 cm^{-1} vw.

When the red filtrate of 1k was allowed to stand overnight at 268 K with an ungreased stopper, the solution color went to yellow as expected for the oxidation of 1a to an iridium(III) diazene complex 5. The solution was precipitated with hexane and the yellow solid 5d-F recrystallized twice from methanol/ether. IR: 3160 m, 3058 m, 2041 vs, 1595 s, 1565 m, 1485 m, 1438 s, 1417 wm, 1393 wm, 1315 wm, 1259 wm, 1228 s, 1194 m, 1165 wm, 1094 vs (with an undefined shoulder corresponding to ν BF$_4$ at lower frequency), 1000 s, 866 wm, 824 wm, 761 m, 746 s, 713 s, 696 vs, 617 vw, 580 m, 567 m, 521 vs, 479 wm, 455 m, 450 sh, 430 wm, 309 cm^{-1} w.

Upon cooling to 268 K, an oil containing much of the [IrH$_2$(CO)(PPh$_3$)$_3$]BF$_4$ separated from methanol/benzene/ether solution of the collected filtrates of the three previous separations.

The supernate was stripped dry, dissolved in propanone/toluene and the solution allowed to evaporate to dryness in an open beaker. A lightly-colored solid formed, imbedded in a brown oily matrix which could be washed away without much loss of the solid if washed with propanone before the oil hardened. This slow crystallization was repeated several times until a clean yellow solid 5d-FBF$_3$ was collected. IR: 3165 m, 3060 wm, 2074 s, 1592 m, 1567 m, 1482 m, 1436 s, 1311 wm, 1256 wm, 1226 s, 1190 m, 1085 vs with very broad low frequency shoulder of completely undefined absorptions, 998 s, 861 wm, 821 wm, 746 s, 709 s, 694 s, 569 wm, 518 vs, 456 wm, 417 w, 312 cm^{-1} w.

After partially stripping and decanting the reaction mixture of a duplicate synthesis, a solid formed in the decantate during further evacuation. The solid was filtered, washed twice with toluene and vacuum dried to a very pale orange solid. This was recrystallized from propanone/toluene as a white solid. MP 473 K. Anal. C, 67.8; H, 5.03; N, 0. Calcd. for PF$_2$Ph$_3$: C, 72.0; H, 5.03. IR: 3067 wm, 1589 m, 1485 m, 1439 vs, 1338 wm, 1314 wm, 1215 sh, 1190 s, 1168 s, 1118 vvs, 1084 vs, 1029 s, 998 s, 928 s, 883 vs, 753 s, 733 vs, 690 vs, 572 s, 543 vs, 525 vs, 510 s, 464 vw, 451 wm, 435 w, 387 cm^{-1} vw. After hydrazido complex had been removed in this preparation, the diazene 5 was obtained by overnight air oxidation at 268 K. Repeated recrystallization from propanone/ ether/hexane and propanone/benzene/ether gave a bright yellow solid which was clearly a mixture of 5d-F and 5d-FBF$_3$. Anal. C, 48.0 with V$_2$O$_5$, 50.4; H, 3.66, 3.78; N, 2.65; F, 14.45. Calcd. for $[Ir(NHNC_6H_3\text{-}4\text{-}F)(CO)FBF_3(PPh_3)_2]BF_4$: C, 49.6; H, 3.52; N, 2.57; F, 16.12. Calcd. for $[Ir(NHNC_6H_3\text{-}4\text{-}F)(CO)F(PPh_3)_2]BF_4$: C, 53.04; H, 3.53; N, 2.88; F, 11.71. IR: ν CO is a flat-bottomed peak from 2070 to 2046 cm^{-1}.

The early-oiling material of this duplicate reaction was neutralized with methanolic KOH, depositing a significant portion (10-20 %) of the $IrH(CO)(PPh_3)_3$ added, identified by infrared, along with much tetrafluoroborate, presumably as a K salt. The filtrate was precipitated with water and $[Ir(CO_2Me)\{N_4(C_6H_4\text{-}4\text{-}F)_2\}(PPh_3)_2]$ recrystallized to a burnt orange solid, first from benzene/ether/hexane and then from propanone/ ether/hexane. Anal. C, 57.8; H, 4.04; N, 4.76. Calcd. for $C_{50}H_{41}N_4F_2IrO_2P_2$: C, 58.8; H, 4.04; N, 5.48. IR: 3050 wm, 2930 vw, 1640 m, 1619 m, 1498 s, 1482 sh, 1433 s, 1311 vw, 1261 w, 1214 s, 1151 m, 1089 s, 1060 m, 1023 m, 913 wm, 815 m, 745 m, 728 wm, 694 s, 634 w, 539 s, 521 s, 460 wm, 420 wm, 396, 382 sh, 316 cm^{-1} vw.

3c. Reaction of Iridium Hydride with $2\text{-}FC_6H_4N_2^+$.

$[Ir(NHNHC_6H_3\text{-}2\text{-}F)(CO)(PPh_3)_2]BF_4$, 1d, was prepared in the manner of 1a from solutions of 3 (554 mg, 0.54 mmole) in toluene (40 ml) and $2\text{-}FC_6H_4N_2BF_4$ (226 mg, 1.1 mmole) in propanone (20 ml). The hydrazido complex was separated from organic impurities in the late-oiling fraction by stirring the vacuum-dried residue in 2 ml methanolic HBF_4, filtering the solid which formed spontaneously at room temperature, washing with ether, and drying in vacuum; yield 58 mg. IR: 3280 wm (ν NH); 3055 w (ν arylH); 2000 s (ν CO); 1560 w, 1480 wm, 1435 m, 1329 s, 1310 w, 1270 w, 1235 m (ν arylF); 1190 m, 1100 sh, 1085 s, 1055 sh (ν BF_4), 1031 sh, 1002 m, 885 wm, 860 vw, 770 sh (δ 1,2,3-substituted aryl); 742 m (δ phenylH); 690 s (δ C-C phenyl); 613, 579, 522 s, 465 w, 425 w, 400 cm^{-1} w. Larger crystals of 1d formed from methanolic HBF_4/propanone by evaporation under a slow flow of nitrogen.

Other products were recovered in small quantity, analytically impure. Addition of ether to an ethanol solution of the early- oiling material until the first sign of separation and cooling at 268 K precipitated a gummy product, which solidified from a propanone/ethanol solution upon slow solvent evaporation to <0.5 ml. Mother liquor was decanted from the orange solid tetrazene 4b; yield 7 mg (1%). IR: 3050 wm (ν arylH); 2050 s (ν CO); 1590 wm, 1493 s, 1482 m, 1454 wm, 1436 s, 1310 w, 1261 m, 1210 wm, 1160 wm, 1085 s, 1055 s, 1000 m, 824 w, 805 w, 744 s, 693 s, 620 w, 537 s, 520 s, 460 w, 420 cm^{-1} w.

The supernate from initial tetrazene separation was treated with LiCl in propanone, with precipitation of iridium complexes by addition of water and vacuum drying. From the benzene soluble fraction of this mixture, a propanone/hexane crystallization produced yellow $[IrCl(NHNC_6H_3\text{-}2\text{-}F)(CO)(PPh_3)_2]BF_4$, identified by comparison of its infrared spectrum with that of previously prepared analogues,[171] and an off-white solid with a curious infrared spectrum (ν NH 3253 w, 3174 w, 3102 sh; ν CH 3050 wm; ν CO 2060 s; 1568 m, 1502 s, 1485 m, 1436 s; ν aryl-F 1252 m, little tetrafluoroborate at 1060; 1,2-subst. aryl ca. 760 sh with no 1,2,3-subst. aryl expected near 785; ν IrCl 335 m, 308 cm^{-1} m), which could not be identified. Anal. C, 45.7; H, 3.40; N, 1.84. Calcd. for $[IrCl_2(CO)(NH_2NHC_6H_4F)(PPh_3)_2]BF_4$: C, 50.2; H, 3.63; N, 2.72. Crystallization from propanone/water by slow evaporation of the benzene-insoluble portion gave a small amount of nearly colorless $[IrH_2(CO)(PPh_3)_3]BF_4$, **8**. Anal. C, 58.9; H, 4.55; N, 0. Calcd. C, 60.3; H, 4.32. IR: (ν CO see Table III-2), 1050 vs (ν BF_4).

3d. Reaction of Iridium Hydride with $3\text{-}FC_6H_4N_2^+$.

$[Ir(NHNHC_6H_3\text{-}3\text{-}F)(CO)(PPh_3)_2]BF_4$, **1h**, was synthesized in the manner of **1a**. Very little was recovered from the crystallization of the late-oiling fraction. For IR see figure II-3. A duplicate synthesis in benzene/propanone produced a large portion of hydrazido complex by infrared of the crude total isolate, but no hydrazide could be solidified even with seeding. No other products crystallized satisfactorily.

3e. Reaction of Iridium Hydride with $2\text{-}CH_3OC_6H_4N_2^+$.

$[Ir(NHNHC_6H_3\text{-}2\text{-}OCH_3)(CC)(PPh_3)_2]BF_4$, **1f**, was synthesized in the manner of **1a** from 306 mg 3 and 133 mg 2-methoxybenzenediazonium tetrafluoroborate in 30 ml benzene and 15 ml propanone respectively. As a result of the change from toluene to benzene, no early-oiling material formed, so vacuum stripping left a single involatile residue. Complex 1f solidified upon addition of 2 ml methanolic HBF_4. To remove all hydrazido complex with this volume of solvent, the bottom of the reaction flask was warmed with water (<320 K) allowing evaporation of the methanol which condensed and carried down the crude product from the walls of the flask. The liquid was decanted and the solid rinsed with 5:1 ether/methanol and ether. MP 448 K dec. IR: 3256 m, 304 wm, 2926 w, 2835 vw, 2000 vs, 1584 w, 1561 m, 1525 sh, 1481 m, 1458 wm, 1435 s, 1395 wm br, 1311 w, 1253 s, 1214 m, 1184 m, 1162 sh, 1146 sh, 1092 vs, 1058 s, 1029 s, 1001 s, 926 w, 870 w, 840 wm, 765 sh, 747 s, 692 vs, 620 wm, 535 sh, 519 vs, 424 wm. Some crystals of 1f were allowed to stand in air and light for 3 months. These showed only very slight surface decomposition to a brown material.

Though impure aryldiazene complex 5 was obtained as an oil, no useful separation could be accomplished from the filtrate of 1f, which had an infrared band near 3200 cm^{-1} m also seen in isolates from $4\text{-}MeOC_6H_4N_2BF_4$. (See below.)

3f. Reaction of Iridium Hydride with $2\text{-}O_2NC_6H_4N_2^+$.

The hydrazido complex 1b was synthesized in the manner of 1a from 3 (502 mg, 0.50 mmole) and $2\text{-}O_2NC_6H_4N_2BF_4$ (236 mg, 1.0 mmole). After about 1 h of vacuum evaporation (with oiling in the final 0.3 h) the color of the remaining liquid appeared distinctly more red than the initial deep violet. At this point the solution was decanted and both portions stripped to dryness. In contrast to most preparations, the hydrazido complex 1b appeared in the early-oiling fraction for this aryl substitution. Violet solid 1b separated from methanolic HBF_4 and was filtered and washed with ether. IR: 3275 m br, 3060 w, 2003 s, 1590 wm, 1550 wm, 1497 m, 1482 m, 1436 m, 1416 wm, 1366 wm, 1333 m, 1284 s, 1252 m, 1210 sh, 1183 m, 1159 m, 1083 s, 1052 s, 997 m, 920 w, 881 wm, 790 w, 739 m, 691 s, 579 w, 518 s, 453 wm, 414 w, 390 cm^{-1} vw.

The filtrate of 1b was combined with late-oiling reaction product and the solution slowly oxidized to light brown solid 5a, obtained from methanol/ ether/hexane with cooling to 268 K. The presence of solvent of crystallization was apparent from the infrared alkyl region. IR: 3142 m, 3059 m, 2950 wm, 2930 wm, 2870 wm, 2057 vs, 1595 wm, 1574 wm, 1532 s, 1484 s, 1437 vs, 1395 wm, 1354 m, 1303 wm, 1226 w, 1192 m, 1175 wm, 1093-1050 vvs, 998 s, 851 wm, 803 wm, 763 sh, 744 s, 710 s, 693 vs, 614 w, 576 m, 514 vvs, 456 m, 435 sh, 417 cm^{-1} sh.

Attempts to purify the crude product of other syntheses by column chromatography failed because material did not move. Some neutral Ir(I) diazene was formed on alumina and eluted, but no analytically pure product was obtained because the developing solvents used (CH_2Cl_2/ethanol) were inappropriate. (The dipropanone solvate[49] of 6, $Ir(CO)Cl_2(NNC_6H_4\text{-}2\text{-}NO_2)(PPh_3)_2$, was obtained upon recrystallizing one fraction eluted. Anal. C, 54.3; H, 4.30; N, 3.79. Calcd. for $C_{49}H_{46}N_3Cl_2IrO_5P_2$: C, 54.4; H, 4.29; H, 3.88.)

3g. Reaction of $IrCl(CO)(PPh_3)_2$ with $2\text{-}O_2NC_6H_4N_2^+$.

$IrCl(CO)(PPh_3)_2$ (201 mg, 0.26 mmole) and 2-nitrobenzenediazonium tetrafluoroborate (62 mg, 0.26 mmole) were ground together, added to a test tube under nitrogen and treated with 5 ml propanone at 213 K with stirring. When the temperature had risen to 228 K, 6 ml ethanol was added. Reaction to give a red color to the solution occurred above ca 258 K. After 1 h total the solution had come to room temperature and was filtered. The dull orange solid was identified as $IrCl_2(N_2C_6H_4\text{-}2\text{-}NO_2)(CO)(PPh_3)_2$ by comparison of its infrared spectrum with an authentic sample.[49] Yield 51 mg, 41% assuming only half the reactant iridium or diazonium can be transformed to this product. The filtrate was evaporated to dryness under vacuum, impurities were extracted with ethanol and then benzene, and the solid 1b redried under vacuum. Yield 45 mg, 36%.

3h. Reaction of Iridium Hydride with $2\text{-}BrC_6H_4N_2^+$.

The hydrazido complex 1e was prepared in the manner of 1a from 3 (492 mg) and $2\text{-}BrC_6H_4N_2BF_4$ (265 mg) in toluene/propanone. When solidification of the hydrazido complex 1e (νNH 3250, νCO 2000 not due to 8 because of the absence of intensity at 2100 cm^{-1}) present in the late-oiling fraction was tried with methanolic HBF_4/ether, the yellow-green complex 9b precipitated which analyzed as a tetrazene isomer: C, 48.8; H, 3.28; N, 4.71. Calcd. for $C_{49}H_{38}N_4BBr_2F_4IrOP_2$: C, 49.1; H, 3.19; N, 4.67. IR: 3054 w, 1667 s (1675 in crude isolate), 1562 wm, 1482 wm, 1460 wm, 1436 m, 1296 w, 1255 w, 1155 sh, 1095 sh, 1050 s, 1032 sh, 999 m, 747 m, 712 s, 693 s, 562 wm, 513 s, 446 w, 420 cm^{-1} w.

When the filtrate was treated with ether/hexane and cooled to 265 K a brown solid formed which was recrystallized thrice from propanone/ether to a bright yellow solid, 5c-F. IR: in addition to broad water bands ca. 3400 and 1700-1600, 3156 wm, 3055 wm, 2052 s, 1586 w, 1568 m, 1535 wm, 1507 vw, 1484 m, 1436 s, 1381 w, 1368 w, 1317 w, 1286 wm, 1219 m, 1204 m, 1183 2m, 1094 vs, 1060 vs, 998 s, 857 wm, 772 m, 746 s, 611 s, 694 vs, 607 vw, 579 m, 529 vs, 461 wm, 376 cm^{-1} vw.

Neutralization of the early-oiling material produced 3 and iridium(I) aryldiazene 10 (See below, Section 4g.).

3i. Reaction of Iridium Hydride with $3\text{-}CH_3C_6H_4N_2^+$.

The hydrazido complex 1i was prepared from 3 (293 mg, 0.29 mmole) and $3\text{-}CH_3C_6H_4N_2BF_4$ (120 mg, 0.58 mmole) in toluene/ propanone in the manner of 1a, but all solvents were stripped from the reaction flask without decanting. The residue was dissolved in methanolic HBF_4 (6 ml) and treated with ether and hexane without formation of a precipitate. The solution was filtered and evacuated to a volume of 3-4 ml, when an orange solid formed, which was filtered and washed with ether and hexane. The solid was recrystallized from minimum neutral methanol by addition of ether/hexane. IR: 3282 m, 3056 wm, 2920 wm, 2850 sh, 1993 vs, 1481 m, 1435 s, 1310 w, 1247 wm, 1219 m, 1184 m, 1087 vs, 1053 sh, 999 s, 849 wm, 800 wm, 745 s, 693 s, 517 vs, 450 wm, 422 cm^{-1} wm. Because of low C analysis another recrystallization was done on this material, which left a filtrate containing 5 (ν NH 3150, ν CO 2055; crystallization attempts were unsuccessful.) and materials absorbing with medium intensity at 1685 and 1645 cm^{-1}. The latter band also appeared in the spectrum of the solid sample of 1i stored six months at room temperature.

After neutralization (excess NaOH in ethanol) of the filtrate of 1i, $IrH(CO)(PPh_3)_3$ was filtered from alcohol. Addition of water to the filtrate precipitated a red-brown material with no ν NH, which absorbed at 1940 cm^{-1} (ν CO). A peak at 775 cm^{-1} and shoulder at 720 cm^{-1} is evidence for 1,2,3-aryl substitution. When purification of this material by chromatography on silica gel (5% ether/toluene) was attempted, the initially separated red band decayed as it was further developed until it had disappeared before elution. It probably was not aryldiazene complex 10, but the material described above (Section B,6) as pseudodiazene.

3j. Reaction of Iridium Hydride with $3\text{-}O_2NC_6H_4N_2^+$.

Synthesis of $[Ir(NHNHC_6H_3\text{-}3\text{-}NO_2)(CO)(PPh_3)_2]BF_4$ from 3 (546 mg) in the manner of 1a was successful in producing crude 1g in both early- and late-oiling fractions, but efforts to obtain solid from a variety of solvent systems with and without cooling was unsuccessful.

Neutralization of the product mixture allowed isolation of 3 and aryldiazene 10. (See below, Section 4e.)

3k. Reaction of Iridium Hydride with $3,5\text{-}(CH_3)_2C_6H_3N_2^+$.

Simultaneous addition of $IrH(CO)(PPh_3)_3$ (249 mg, 0.25 mmole) and $3,5\text{-}(Me)_2C_6H_3N_2BF_4$ (108 mg, 0.49 mmole) in toluene and propanone respectively over 0.2 h gave a clear red solution which was stripped to dryness without decanting. The infrared of the crude material showed no residual diazonium salt (ν NN at 2280 cm^{-1}) or 3 (ν CO at 1925 cm^{-1}), and no arylhydrazido complex 1 (ν NH ca. 3280 cm^{-1}), but had three strong carbonyl bands at 2100, 2000 ($[IrH_2(CO)(PPh_3)_3]BF_4$), and 2040 cm^{-1}.

Neutralization of this mixture with ethanolic KOH slowly precipitated a mixture of $IrH(CO)(PPh_3)_3$ (ν CO 2075, 1925 cm^{-1}) with materials absorbing at 1955 cm^{-1} and 1300 wm, 1050 vvs (ν BF_4). This was dissolved in hot toluene, leaving KBF_4 as a white solid: readily soluble in water, did not melt <525 K, did not burn or char in a flame. The toluene solution was cooled (268 K) overnight but no solid formed until addition of a large excess of methanol. The yellow precipitate was identified as $IrH(CO)(PPh_3)_3$ by infrared (ν IrH 2075, ν CO 1928 cm^{-1}).

3l. Reaction of Iridium Hydride with $4\text{-}CH_3C_6H_4N_2^+$.

Syntheses of hydrazido complexes 1 from $IrH(CO)_2(PPh_3)_2$, 2, were also done by simultaneous addition of both the hydrazide and diazonium salts, but with only one mole diazonium salt. For example,

$4\text{-}CH_3C_6H_4N_2BF_4$ (21 mg, 0.10 mmole) in degassed propanone (10 ml) and 2 (79 mg, 0.10 mmole) in degassed benzene (10 ml) were added dropwise under nitrogen to the stirred mixture at room temperature over 0.1 h. The solution color remained yellow until near the end of addition but over 0.3 h a full redness developed. All solvents were stripped, then 1 ml methanolic HBF_4 used to dissolve the residue. Addition of 6 ml ether increased the amount of precipiated white solid $IrH_2(CO)_2(PPh_3)_2]BF_4$, 7, which was filtered and washed with ether; yield 14.2 mg, 16%. IR: see Table III-1 and Section 3m.

Addition of hexane to the filtrate deposited an oil so all volatiles were again stripped and 0.8 ml fresh methanolic HBF_4 added. Orange solid 1ℓ formed; 4 ml ether were added, the solid was filtered, drained well without washing, and vacuum dried. MP ca. 405 K dec. Recrystallization did not remove a trace of 5e. IR: 3276 s, 3170 sh (ν NH of impurity); 3056 m 2917 w, 2034 (ν CO impurity), 1996 vs, 1587 m, 1566 m, 1481 s, 1434 s, 1396 wm, 1310 m, 1276 wm, 1255 wm, 1220 m, 1187 m, 1161 m, 1086 vs, 1055 vs, 997 s, 879 w, 845 w, 796 wm, 745 s, 693 vs, 615 w, 583 vs, 565 wm, 556 sh, 517 vvs, 466 wm, 450 wm, 432 m, 390 w.

The filtrate of 1ℓ in a side-arm tube was treated with hexane until just cloudy, then 0.2 ml methanol to reclarify the solution and placed in the freezer without greasing the stopper. The solution slowly lost redness and deposited yellow solid 5e; yield 12 mg, 12%. IR: 3161 m, 3053 m, 2920 wm, 2848 sh, 2037 vs, 1591 m, 1483 m, 1432 s, 1399 m, 1309 m, 1269 wm, 1223 m, 1208 wm, 1189 m, 1169 wm, 1087 vs, 1057 vs, 997 s, 884 wm, 866 w, 807 w, 745 s, 708 s, 693 vs, 614 vw, 584 wm, 565 m, 515 vs, 457 m, 436 cm^{-1} m.

Neutralization by excess methanolic K_2CO_3 of the material not collectable from recrystallization of 1ℓ gave a red solution which deposited a purple-maroon solid, especially after addition of water. The solid was filtered and washed thrice with 4:1 methanol/water and once with water. Anal. C, 49.6; H, 3.89; N, 1.61. This corresponds to a C:H:N: ratio of 72:67:2. IR: 3285 vvw (ν NH), 1958 m (ν CO). (See discussion of pseudodiazene, Section B 6.)

A relatively large scale reaction of $4\text{-}CH_3C_6H_4N_2BF_4$ with 3 (370 mg) was done like the synthesis of 1a but in benzene/propanone so that both solvents came off together under vacuum and no preliminary separation was accomplished. The crude, dry residue did not seem to have much hydrazido complex in it by infrared and when 2 ml methanolic HBF_4 was added no precipitate formed until the solution was concentrated to about 1 ml and 4 ml ether were added. This solid was a mixture with only low iridium carbonyl intensity at 2040 cm^{-1} and was discarded. From the filtrate a mixture of tetrazene 4 and diazene 5 separated from methanol/ether at 268 K. The diazene was purified by repeated crystallization from propanone/ether using too little propanone to completely dissolve the solid, since it was hard to get solid to separate without seeding. After removing diazene the tetrazene 4d was crystallized from propanone/ether. IR: 3058 wm, 2921 w, 2867 vw, 2026 vs, 1586 wm, 1504 s, 1482 m, 1435 s, 1316 w, 1266 wm, 1235, 1214 wm, 1187, 1179 wm, 1160 m, 1091 vs, 1057 vs, 1010 sh, 999 m, 923 w, 820 m, 744 s, 690 s, 638 vw, 609 vs, 561 m, 530 s, 515 s, 497 m, 422 cm^{-1} wm. Because of difficulty in obtaining pure samples, the yields of 4d and 5e by this method were less than 2%.

3m. Reaction of Iridium Hydride with 2-$CF_3C_6H_4N_2^+$.

Attempted synthesis of 1c from 2 in the manner of 1ℓ (Section 31) with addition done over two minutes or 0.5 h gave a brown isolate which by infrared contained little or no hydrazide complex 1c. The first material to separate from methanol/ether was 7. Anal. C, 52.8; H, 3.75; N, 0. Calcd. for $[IrH_2(CO)_2(PPh_3)_2]BF_4$: C, 53.0; H, 3.74. IR (Nuj): 3065 wm, 2071 wm, 2021 vs, 1999 vs, 1585 vs, 1480 m, 1435 s, 1305 w, 1183 wm, 1165 wm, 1095 vs, 1056 vs, 996 m, 754 m, 712 s, 688, 679 s, 550 w, 517 vs. In KBr a peak of medium intensity is seen at 350 cm^{-1}. The carbonyl region is nearly duplicated (See also Section III,B,2) if scanned very quickly after preparation of the salt mull, but a peak at 2030 cm^{-1} grew in quickly and after standing overnight the spectrum had two peaks at 2000 m and 1929 cm^{-1} s. When a propanone solution was loaded into a salt cell to observe the carbonyl region, there was an extremely vigorous bubbling lasting only seconds, and the spectrum was similar to that in KBr after long standing.

Addition to the filtrate of 7 of more ether and cooling gave impure diazene 5b, which was recrystallized from methanol/ether/hexane with cooling to bright yellow crystals. The presence of nonstoichiometric ether not removed at high vacuum was shown by both infrared and PMR; the analyses suggested 0.25-0.3 mole. IR: 3142 wm, 3060 wm, 2951 w, 2931 w, 2868 vw, 2056 s, 1584, 1574 wm, 1484 m, 1437 s, 1393 wm, 1314 s, 1302 sh, 1224 m, 1136 s, 1090 vs, 1075 sh, 1060 sh, 998 s, 858 w, 817 w, 798 wm, 743 m, 708 m, 693 s, 576 wm, 516 s, 456 cm^{-1} m.

Synthesis of $[Ir(NHNHC_6H_3\text{-}2\text{-}CF_3)(CO)(PPh_3)_2]BF_4$ was attempted from 3 in the manner of 1a. Infrared spectra of both early- and late-oiling residues indicated the presence of appreciable amounts of 1c, with the late-oiling material being slightly richer. When methanolic HBF_4 was added to this a green solid 9a formed. (Analysis in Table III-3) It was very soluble in propanone, $CHCl_3$; soluble in methanol, ethanol; sl. soluble in benzene, ether; insoluble in water, hexane. Upon heating in air it decomposed above ca. 433 K without melting; above 473 K it decomposed with rapid evolution of gas and reformed into a solid. The solid decomposed overnight during attempted crystallization from propanone/methanol under slow N_2 flow. IR: 3058 w, 1679 s, 1599 wm, 1573 m, 1480 m, 1435 s, 1315 s, 1269 m, 1177 s, 1138 vs, 1097 s, 1048 vs, 1036 sh, 998 m, 778 m, 745 m, 712 m, 693 s, 650 m, 580 w, 513 s, 421 vw, 321 cm^{-1} vw.

Further attempts to isolate 1c from the combined residues of the reaction were unsuccessful, only $[Ir(NHNC_6H_3\text{-}2\text{-}CF_3)(CO)F(PPh_3)_2]BF_4$ separated so the crude hydrazide was neutralized to 10. (See Section 4d.)

3n. Reaction of Iridium Hydride with $4\text{-}CH_3OC_6H_4N_2^+$.

$[Ir(NHNHC_6H_3\text{-}4\text{-}OMe)(CO)(PPh_3)_2]BF_4$, 1m, was synthesized from 2 (111 mg) by the method described for 1 . After white solid $[IrH_2(CO)_2(PPh_3)_2]BF_4$ (21 mg, 17%) was collected, addition of hexane gave an oil. When, without decanting, solvents were almost completely removed under vacuum, the residue turned yellow. Addition of ether and water gave return to redness. The liquids were poured off and the remaining crude 1m vacuum dried. IR: ν NH, 3285, 3228 sh; ν CO 1993 cm^{-1}.

Some 1m was allowed to oxidize in propanone/ether and yellow solid 5f precipitated with excess ether. IR: 3190 wm, 3058 wm, 2047 s, 1590 s, 1557, 1541 wm, 1482 m, 1437 s, 1384 wm, 1330 2m, 1285 m, 1246 s, 1188, 1179 wm, 1162 wm, 1120 sh, 1090 s, 1060 s, 1035 s, 998 m, 870 wm, 845 w, 817 w, 759 sh, 746 m, 709 sh, 695 s, 612 w, 576 wm, 515 s, 455 wm, 430 cm^{-1} wm.

The synthesis was also attempted at 233 K by intimately mixing 2 (85 mg, 0.11 mmole) and $4\text{-}CH_3OC_6H_4N_2BF_4$ (25 mg, 0.11 mmole) and condensing degassed propanone in under vacuum. Reaction is visible at 213 K both by evolution of gas and color change to orange. After 3.6

h the solution was allowed to warm as volatiles were removed under vacuum. Methanolic HBF_4/ether allowed solidification of both $IrH_2(CO)_2(PPh_3)_2]BF_4$, 7, and $[Ir(CO)\{N_4(C_6H_4\text{-}4\text{-}OMe)_2\}(PPh_3)_2]BF_4$, 4e. These were separated by recrystallization from propanone/benzene. Each was identified by analysis and infrared: values for 7 agree with those reported above; 4e IR: 3058 wm, 2837 w, ca. 2040 sh, 2030 s, 1600 s, 1585 m, 1503 vs, 1481 m, 1434 s, 1301 m, 1250 s, 1185, 1179 sh, 1168 m, 1087 vs, 1057 vs, 1038 sh, 1000 m, 835 m, 746 m, 695 s, 565 wm, 534 m, 520 cm^{-1} s.

Attempted synthesis of 1m in a manner similar to 1a using 181 mg of 3 was successful in producing appreciable crude hydrazido complex in the decantate (identified by infrared: ν NH 3285; ν CO 1990 cm^{-1}). An attempt to precipitate 1m by addition of NH_4BF_4 was unsuccessful and the methanol solution was largely precipitated with water and dried. Samples of yellow materials spectroscopically identified as 5f (e.g. ν NH 3183, ν CO 2040, δ CH of 1,2,4-aryl 866, 846, 803) were recovered from the filtrate and precipitate above as well as from the early-oiling reaction residue, but these had widely varied decomposition temperatures (433 and 473 K) and irrational analyses: C, 52.4, 49.5; H, 3.91, 3.81; N, 2.56, 2.62. Calcd. for $[Ir(NHNC_6H_3\text{-}4\text{-}OMe)(CO)F(PPh_3)_2]BF_4$: C, 53.6; H 3.78; N, 2.84. Calcd. for $[Ir(NHNC_6H_3\text{-}4\text{-}OMe)(CO)FBF_3(PPh_3)_2]BF_4$: C, 50.2; H, 3.54; N, 2.66.) and were atypically unstable during attempted recrystallization. The early-oiling residue from this synthesis also seemed to contain peculiar products. For instance, after the residue was dissolved in dilute methanolic HBF_4 and the diazene **5f** (noted above) precipitated with benzene/hexane, addition of excess hexane caused separation of an impure, red oil with a relatively intense νNH at 3202 m, νCO 2070 and a band at 1507 m(tetrazene?), and δCH of 1,4-aryl at 836 cm^{-1} m.

3o. Products from $4\text{-}NO_2C_6H_4N_2BF_4$

Synthesis of **1j** (detected by νNH 3260 cm^{-1}) was accomplished using **2** and $4\text{-}O_2NC_6H_4N_2BF_4$ in benzene and propanone in the manner of **1ℓ** above, however it could not be separated before decomposition to a yellow solid presumed to be FBF_3 diazene from νCO at 2075 cm^{-1}. Attempted recrystallization of this from propanone/toluene gave a chocolate oil; nothing was recovered.

Attempted synthesis of **1j** by addition of dimethylformamide (4 ml) to a mixture of $IrH(CO)_2(PPh_3)_2$, **2**, (81 mg) and $4\text{-}O_2NC_6H_4N_2BF_4$ (25 mg) gave a crude reaction product with no νNH apparent and hydride or carbonyl absorptions about 2140, 2080, 2040, 1970, and 1925 cm^{-1}. No pure materials were isolated from this, though methanolic HBF_4 allowed separation of an oil containing $[IrH_2(CO)_2(PPh_3)_2]BF_4$ of stereochemistry C (See Section III B **2**, trans phosphines); IR includes νCO: 2140, 2075 sh, 2040 cm^{-1}. The 1925 cm^{-1} absorption probably comes from decomposition of a dihydridic cation to $IrBr(CO)_2(PPh_3)_2$ in the KBr matrix.

Attempted synthesis of $[Ir(NHNHC_6H_3\text{-}4\text{-}NO_2)(CO)(PPh_3)_2]BF_4$ from **3** (577 mg) in the manner of **1a** with addition over 0.5 h was distinctly unsuccessful in that neither crude fraction contained appreciable **1j**. Although the late-oiling material displayed some νNH intensity near 3270 cm^{-1}, there was very little IrCO infrared absorption compared to the intensity of the phenyl modes (e.g. less than the intensity at 1480 cm^{-1}). Early-oiling material seemed to have an unusually large amount of $[IrH_2(CO)(PPh_3)_3]BF_4$ from infrared absorption at 2100 cm^{-1}. No products were isolated.

4. Preparations of $Ir(NHNC_6H_3G\text{-}C^6,N^1)(CO)(PPh_3)_2$, **10**.

a. Preparation of $Ir(NHNC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2$.

The aryldiazene complex **10a** was synthesized by addition of 4.53 ml of 9.66 mM NaOH (43.8 microequivalents) degassed aqueous NaOH to 43 mg **1b** (43.8 microequivalents) in propanone. The solution color became purple but no solid precipitated until addition of water, which was done so fast that a colloid formed. The colloid was collected, vacuum dried, dissolved in benzene and freeze dried. IR: 3280 w, 3050 wm, 2921 w, 2855 sh, 1960 vs, 1585 wm, 1572 w, 1511 m, 1480 m, 1435 s, 1408 wm, 1335 m, 1265 s, 1225 m, 1186 m, 1161 wm, 1118 wm, 1090 m, 1029 wm, 1000 wm, 861 wm, 789 wm, 769 wm, 745 m, 695 s, 619 vw, 591 w, 541 sh, 521 s, 460 w, 426 cm^{-1} w. PMR ($CDCl_3$): 12.7 br s, NH; 7.9-6.55 complex, aryl, phenyl and $CHCl_3$.

Addition of concentrated KOH in water to a solution of 10a in propanone gave no further color change. A solution allowed to stand in air became slightly more reddish, but did not discolor. When the solid was allowed to stand in a loosely stoppered flask decomposition occurred, giving a material with carbonyl stretching frequencies at 2020, 1960, and 1948 cm^{-1}. The former is probably due to the presence of an iridium(III) complex and the latter to the material referred to as pseudodiazene.

4b. Preparation of $Ir(NHNC_6H_3\text{-}4\text{-}F)(CO)(PPh_3)_2$.

When $[Ir(NHNHC_6H_3\text{-}4\text{-}F)(CO)(PPh_3)_2]BF_4$, 1k (21 mg, 22 micromole) was treated with 0.05 M methanolic K_2CO_3 (0.6 ml), the orange solid dissolved to give a dark red solution and then reprecipitated to leave an orange solid in a slightly pink solution. After 3 ml water were added the solution pH was 6.5 on narrow range pH test paper. The orange solid 10d was filtered and washed with water. IR: 3287 vw (3283 in $CHCl_3$); 3051 w, 1953 s (1961 in $CHCl_3$); 1588 m, 1533 w, 1479 wm, 1434 m, 1280 m, 1240 wm, 1221 wm, 1183 m, 1158 w, 1089 m, 1025 wwm, 998 w, 892 w, 860 w, 827 vw, 808 w, 741 m, 693 s, 580 w, 513 s, 451 wm, 431 wm, 418 wm. PMR ($CDCl_3$): 12.0 br s (with ^{15}N d, J=81 Hz); 8.2-6.4 complex, aryl, phenyl, and $CHCl_3$. The ^{15}N analogue was prepared similarly by neutralizing a mixture of 1k and $[IrH_2(CO)_2(PPh_3)_2]BF_4$.

4c. Preparation of Ir($NHNC_6H_3$-2-F)(CO)(PPh_3)$_2$.

Upon addition of 2-$FC_6H_4N_2BF_4$ (61 mg, 0.29 mmole) in propanone (3 ml) to 3 (140 mg, 0.14 mmole) in toluene (8 ml) at room temperature under N_2, the solution immediately turned brown and then went to a clear, deep red. After stirring for two hours the solution was cooled to 200 K and 0.2 ml Et_3N (1.4 mmole) was added, which gave a darker red color to the solution. All volatiles were removed under vacuum at 273 K and the residue extracted with 7 ml benzene in four portion. The extract was centrifuged, filtered to remove all solid, and then freeze-dried. The isolate was not sufficiently soluble in ether to allow effective crystallization, but with 0.5 ml toluene and 6 ml ether the solid was difficult to precipitate at ca. 210 K. So the material was merely triturated with hexane. Analysis not performed. IR: 3287 vw, 3057 wm, 1956 s, 1596 w, 1526 wm, 1479 m, 1434 s, 1306 sh, 1272 m, 1235 m, 1183 wm, 1157 w, 1116 wm, 1083 m, 1025 w, 996 w, 893 m, 766 wm, 631 m, 717 wm, 691 s, 598 w, 530 s, 510 s, 450 w, 416 cm^{-1} wm. The solid had decomposed completely in six months stored in a screw-cap vial under air, but was moderately stable in air for short periods. Solutions are quite air-sensitive.

4d. Preparation of Ir($NHNC_6H_3$-2-CF_3)(CO)(PPh_3)$_2$.

After repeated attempts at crystallization of [Ir($NHNHC_6H_3$-2-CF_3)(CO)(PPh_3)$_2$]BF_4 (See above, Section 3m), a reaction mixture from IrH(CO)(PPh_3)$_3$ and 2-$CF_3C_6H_4N_2BF_4$ was treated with 4 ml 0.1 M methanolic KOH, making the solution basic.

Red-orange solid $[Ir(NHNC_6H_3\text{-}2\text{-}CF_3)(CO)(PPh_3)_2]$, analytically impure 10b, was filtered from the methanol, washed and well triturated with water until no BF_4^- could be detected in the infrared of the solid. More red solid could easily be precipitated from methanol by addition of water and, though this contained little aryldiazene 10b (by infrared in the ν NH region), it was combined with the material above for a chromatographic separation.

A 2.3x9 cm column of silica gel was prepared under N_2 using benzene, the crude aryldiazene complex loaded as a benzene solution and the column developed with degassed benzene. The bands in order of elution were: a yellow band well separated from the aryldiazene and discarded, a mixture of 10b and pseudodiazene looking violet-red at the bottom and orange-red at the top of the band, well separated from a faint pink (probably orthometalated iridium(III)diazenido complex $[Ir(NNC_6H_3CF_3)(CO)F(PPh_3)_2]$), above which are yellow, black, and brown bands which were washed off with methanol.

The 10b/pseudodiazene eluate was reduced to an oil under vacuum and triturated with hexane and ether. The hexane decantate was red. The solid was left with an impurity, quite obvious from alkane and carbonyl infrared absorptions at 2955, 2910, 1850 sh, and 1715 cm^{-1}, whose origin was traced to the benzene. Ether trituration gave a near colorless decantate and left pure 10b. IR: 3278 wm, 3048 wm, 1958 sh, 1943 vs, 1582, 1572 vw, 1480 m, 1434 s, 1315 s, 1280 s, 1240 m, 1204 m, 1184 wm, 1161 m, 1123 s, 1089 s, 1067 m, 1049 m, 1026 wm, 998 wm, 869 wm, 822 wm, 777 m, 744 m, 721 wm, 694 s, 624, 617 vw, 581 wm, 534 m, 517 s, 485 m, 459 wm, 417 cm^{-1} wm. The solid readily decomposed in the Raman beam. Decomposition in a KBr pellet in air over three days gave a decrease in νNH and increase at 720 and 540 cm^{-1}.

4e. Preparation of $Ir(NHNC_6H_3\text{-}3\text{-}NO_2)(CO)(PPh_3)_2$.

Neutralization of crude isolates from syntheses of 1g (Section 3j) with 0.1 M methanolic KOH and precipitation with water gave a red-brown solid. $IrH(CO)(PPh_3)_3$ was separated by filtration of a propanone solution of the crude aryldiazene complex 10c. Further purification of 10 by selective precipitation was unsuccessful. The impure sample of aryldiazene complex was therefore chromatographed on vacuum-degassed silica gel using degassed toluene to make and load the column (1.3x16 cm) and initially develop it. A yellow-brown material was readily eluted followed by a deep-red band. Because the column was so long, solvent mixture of 4:1 toluene:ether was used to hasten the movement on this band. No solid formed during vacuum evaporation of toluene/ether, but addition of ether to the dried residue gave insoluble purple 10c. IR: 3278 w, 3253 wm, 1965 s, 1579 wm, 1480 m, 1435 s, 1331 s, 1264 wm, 1241 wm, 1181 w, 1159 w, 1090 m, 1025 wm, 998 w, 765 sh, 742 s, 695 s, 535 sh, 517 s, 459 w, 422 cm^{-1} w. A sample precipitated from ether/hexane had an additional shoulder at 1498 cm^{-1}.

4f. Preparation of Ir($NHNC_6H_3$-4-NO_2)(CO)(PPh_3)$_2$.

The standard reaction (Section 31) of 110 mg 2 and 34 mg 4-$O_2NC_6H_4N_2BF_4$ was done in benzene/propanone and the volatiles removed under vacuum. The maroon residue was treated with 2.8 ml methanolic 0.05 M K_2CO_3, which gave a blue solution and purple solid. The solution was stirred to allow full reaction, filtered, and solid 10 washed twice with 1:1 methanol/water. The first washing was clearly blue, the second a clear yellow. These washings, added to the filtrate, caused precipitation of a blue solid, also filtered and washed with methanol/water. The first solid clearly contained aryldiazene 10 from νNH at 3280, νCO 1965; the second did not. Ether did not separate the impurities from the aryldiazene, so it was chromatographed (degassed silica gel, 1.3x15 cm, prepared with degassed benzene) first with benzene, then 3% ether in benzene. The band on the column appeared purple but the solution was blue as eluted and ether trituration gave complete solution, which is not characteristic of 10, but is typical of pseudodiazene. Though the aryldiazene was lost, it did not necessarily convert to pseudodiazene, since both were present before chromatography. The pseudodiazene could not be separated from oily impurity and was lost during attempts to do so.

4g. Preparation on Ir($NHNC_6H_3$-2-Br)(CO)(PPh_3)$_2$.

The aryldiazene complex Ir($NHNC_6H_3$-2-Br)(CO)(PPh_3)$_2$ was similarly prepared by neutralization, using 0.1 M KOH in ethanol, of the early-oiling fraction of an attempted synthesis of 1e (Section 3h).

$IrH(CO)(PPh_3)_3$ first precipitated slowly from the ethanol and was removed by filtration. Addition of water then precipitated a maroon product which contained the aryldiazene and some KBF_4 (broad absorption centered about 1050 cm^{-1}). The sample was chromatographed on silica gel (1.4x30 cm prepared with degassed toluene under N_2) using degassed toluene then 5% ether in toluene to develop and elute a dark red band. The infrared of the material obtained by stripping off toluene and then freeze-drying from benzene had, in addition to absorptions of **10**, those from the non-volatile residue (2920, 2850, 1720 cm^{-1}). The sample was allowed to stand in a covered flask before further work was attempted (18 weeks) and by this time the sample had decomposed. IR peaks common to the water precipitate and the chromatographed sample and thus assigned to **10** appeared at: 3280 wm, 3058 m, 2000 sh, 1955 vs, 1585 w, 1571 wm, 1480 m, 1433 s, 1388 vw, 1273 s, 1229 m, 1188 m, 1159 wm, 1119 m, 1090 s, 1062 m, 1028 wm, 998 wm, 864 m, 770 m, 743 s, 695 vs, 617 w, 588 wm, 576 w, 515 vs, 454 wm, 420 cm^{-1} m.

5. Reactions of $Ir(NHNHC_6H_3G)(CO)(PPh_3)_2$, **1**.

a. Reaction of **1** and **4** with LiCl - Anion Exchange

$[Ir(NHNHC_6H_4)(CO)(PPh_3)_2]BF_4$, **1a**, (9 mg) and LiCl (30 mg) were stirred 0.1 h in 1 ml degassed methanol under N_2 and the volatiles removed under vacuum. The solid was triturated twice with 2 ml water, filtered, and vacuum dried. The infrared was very similar to that of **1a**, but with the expected lowering of BF_4 intensity at 1050, a shoulder at 1959 assigned to the presence of some Ir(I) aryldiazene 10, and slight absorption at 2045 cm^{-1} from Ir(III) aryldiazene 5. Within ten days the red color of the solid in a vial nominally under nitrogen had disappeared; the infrared showed almost no absorption at 1996 cm^{-1} from the carbonyl of 1a, though the carbonyls of the iridium-(I) and -(III) diazenes were apparently unaffected. A solution of $[Ir(CO)\{N_4(C_6H_4\text{-}2\text{-}F)_2\}(PPh_3)_2]BF_4$ in methanol was treated with a large excess of LiCl and 5 d 48% aqueous HBF_4. The tetrazene complex was recovered by addition of water to cloudiness and cooling to 268 K. The infrared spectrum showed no significant change (ν CO 2044 vs. 2040 cm^{-1} before reaction).

5b. Reactions of 1 with Elemental Halogens

When $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$, 1b, (98 mg, 0.10 mmole) in 3 ml methanol was treated with a stoichiometric amount of freshly prepared 0.084 M Br_2 in water (standardized with $Na_2S_2O_3$), the very intensely colored reddish solution lost much of its color quickly. As there was some color left, more bromine was added to a total volume of 1.53 ml, but the final portion of color was not quickly removed. The solution was completely evacuated under vacuum at 2 room temperature to a yellow solid with brown impurities. This impure 5a-Br, $[IrBr(NHNC_6H_3NO_2)(CO)(PPh_3)_2]BF_4$, was washed with water, benzene, and ether and recrystallized from CH_2Cl_2/hexane. (Analysis in Table III-4) IR: 3143 wm, 3051 wm, 2060 w, 1589 m, 1527 s, 1483 s, 1434 s, 1399 m, 1352 s, 1309 m, 1209 m, 1192 sh, 1163 m, 1040 br s, 998 s, 854 m, 802 m, 745 vs, 695 vs, 618 vw, 579 s, 521 vs, 463 m, 442 cm^{-1} sh.

Oxidation by iodine was conducted by adding a benzene solution of the halogen to a methanolic solution of a sample of 1b (10 mg, 10 micromoles) of unknown purity prepared by Dr. Farrell. Addition was stopped when the solution color, which had gone from red to orange-yellow, started to darken to brown; 7 micromoles I_2 used. The solution was stripped to dryness and recrystallized from propanone/hexane to a reddish solid. Anal. C, 45.7; H, 3.48; N, 3.35. Calcd. for $[IrI(NHNC_6H_3NO_2)(CO)(PPh_3)_2]BF_4$: C, 46.6; H, 3.09; N, 3.79. This formulation does not account for the infrared evidence of some substitution of I_3^- for BF_4^- (shoulder of peak at 1087 has no inflection ca 1060 cm^{-1} as did samples with only BF_4^- counterions.). Characteristic IR: ν NH 3155 w, νCO 2060 s, ν NO_2 1532, 1346 cm^{-1}.

Reaction with HI in ether (freshly prepared by extraction of the acid from 47% aqueous solution) gave the same product, presumably due to inadvertent oxidation of HI by air since the ether solution was yellow.

Oxidation by a 6% excess of Cl_2 in benzene proceeded similarly but the yellow-brown product was precipitated from a solution treated with 48% aqueous HBF_4 which was not removed under vacuum.

Anal. C, 42.9; H, 3.47; N, 3.03. Calcd. for $[Ir(NHNC_6H_3NO_2)(CO)Cl(PPh_3)_2]BF_4$: C, 50.8; H, 3.37; N, 4.13. Characteristic IR: νNH 3150 w, νCO 2070 s, νNO_2 1533 m, 1350 m; νIrCl 300 cm^{-1} w. In another trial a ten-fold excess of Cl_2 was added at room temperature, and then the discolored solution evacuated to dryness, leaving a yellow solid. Addition of methanolic HBF_4 left white insoluble $Ir(C_6H_4NO_2)(CO)Cl_2(PPh_3)_2$. Anal. C, 54.3; H, 3.96; N, 1.43. Calcd. C, 54.5; H, 3.95; N, 1.44. Characteristic IR: νCO 2040, νNO_2 1536, 1364, no νBF_4, νIrCl 346, 284 cm^{-1} uncertain because vvw.

5c. Reactions of **1** and **5** with HBF_4 and HX

Treating $[Ir(NHNHC_6H_3\text{-}2\text{-}F)(CO)(PPh_3)_2]BF_4$, **1d**, in methanolic HBF_4 with two moles LiBr for 0.1 h, precipitating with ether and washing twice each with ether and water produced no reaction detected visually or by infrared of the isolate except loss of νBF_4^- intensity, presumably due to anion exchange with bromide.

When $[Ir(NHNHC_6H_3\text{-}2\text{-}F)(CO)(PPh_3)_2]BF_4$ (9 mg) did not visibly react at room temperature with LiBr (1 mg) in methanolic HBF_4 (0.4 ml), more LiBr (ca. 5 mg) and methanolic HBF_4 (0.4 ml) were added and the solution stirred at ca. 320 K. The orange solid previously present turned yellow-tan. Ether (1 ml) was added, the solution filtered and the solid washed twice with ether. The solid was identified as $IrBr_2H(CO)(PPh_3)_2$ by analysis: C, 48.8; H, 3.44; N, 0. Calcd. C, 49.1; H, 3.45. Characteristic IR: νIrH 2225, νCO 2035 sh, 2020 cm^{-1}. After the dried filtrate had been extracted with ether to remove any possible $IrBr_2H(CO)(PPh_3)_2$, the waxy solid remaining had no apparent infrared absorption except ν BF_4 and H_2O bands.

When $[Ir(NHNC_6H_3\text{-}2\text{-}F)(CO)(PPh_3)_2]BF_4$ was treated with LiCl and methanolic HBF_4 for 0.5 h at room temperature the yellow solid recovered after water trituration had an infrared spectrum corresponding to that of the reactant complex except for lower BF_4 intensities at 1050 and 520 cm^{-1}. The same sample was then refluxed 0.2 h with 1.5 ml methanolic HBF_4 and 10 mg LiCl without formation of any $IrCl_2H(CO)(PPh_3)_2$ or further change in the infrared of the isolated solid.

The sample of $[Ir(NHNHC_6H_3\text{-}2\text{-}F)(CO)(PPh_3)_2]^+$ with mixed bromide and tetrafluoroborate counterion, prepared as described three paragraphs above, was allowed to air oxidize in propanone solution to $[IrBr(NHNC_6H_3\text{-}2\text{-}F)(CO)(PPh_3)_2]^+$ (Characteristic IR: ν NH ca. 3160, ν CO 2053, γ aryl-F 1253, δ 1,2,4-aryl 888, 782 cm^{-1}), then treated 0.5 h with LiBr and methanolic HBF_4. The brown solid filtered from the reaction mixture contained $[IrBr(NHNC_6H_3\text{-}2\text{-}F)(CO)(PPh_3)_2]^+$ from comparison of its infrared spectrum with that above.

Addition of 4.00 ml of 0.045 M HBr in ether to 75 mg 1b (76 micromoles) in methanol (3 ml) under N_2 gave no easily seen color change. When the addition was complete a solid was visible, but this as not precipitated in sufficient quantity to allow collection so all volatiles were removed under vacuum and the residue crystallized from propanone/ether at 273 K. The maroon solid was washed with ether and vacuum dried. Characteristic IR: ν NH 3360 br sh, 3160 ; νCO 2061; propanone of solvation 2930, 2847, 1724 cm^{-1}. Anal. C, 49.5; H, 4.03; N, 3.35. Calcd. for $[IrBr(NH_2NHC_6H_3NO_2)(CO)(PPh_3)_2]BF_4$ Me_2CO: C, 49.3; H, 3.77; N, 3.75. The combined reaction products were recrystallized from thf/hexane to obtain a solvent-free complex. Anal. Found: C, 46.2; H, 3.37; N, 3.71. Calcd. C, 48.6; H, 3.32; N, 3.95.

When 0.02 ml of a 0.416 M solution of gaseous HCl in ether was added in two portions to $[Ir(NHNHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$, 1b (26 mg, 26 micromoles) in 4 ml methanol, no reaction was at all apparent. The solution was stirred 0.2 h and evacuated under vacuum. When the volume was reduced, a yellow solid was first formed and then a brown dry residue containing $[IrCl(NH_2NHC_6H_3\text{-}2\text{-}NO_2)(CO)(PPh_3)_2]BF_4$. Characteristic IR: see text, end of Section B7.

6. Reactions of $RhH(CO)(PPh_3)_3$ and $IrH(dppe)_2$ with Diazonium Salts.

a. $RhH(CO)(PPh_3)_3$ Reaction

The reaction of 2 equivalents $2\text{-}FC_6H_4N_2BF_4$ with $RhH(CO)(PPh_3)_3$ in the manner of 1a gave, in the brown, early-oiling product mixture, material which absorbs very broadly about 3160 (ν NH) and 1990 (ν CO of a cationic Rh(I) complex) but not above 2000 cm^{-1}.

When done with $4\text{-}MeOC_6H_4N_2BF_4$ in benzene/propanone and the yellow brown solution evacuated to dryness without decanting, the crude brown product had a distinct νNH at 3180 cm^{-1} and carbonyl absorptions only at 2000 and 1975 cm^{-1}. A peak at 1505 cm^{-1} is possibly indicative of a tetrazene complex.

6b. Reaction of $IrH(Ph_2PCH_2CH_2PPh_2)_2$.

A solution of $2\text{-}O_2NC_6H_4N_2BF_4$ (20 mg, 84 micromole) in propanone (3 ml) was added to $IrH(dppe)_2$ (84 mg, 85 micromole) in toluene (8ml) while stirring at 200 K under argon. The mixture was stirred for 0.3 h and filtered. The orange solid was identified as $IrH(dppe)_2$ by comparison of its infrared with that of the reactant. The filtrate was partially stripped, an orange-tan solid filtered out, washed with toluene, and vacuum dried. Anal. C, 55.5; H, 4.32; N, 0. Calcd. for $Ir(dppe)_2BF_4$: C, 58.0; H, 4.50.

The same reaction was also done in ethanenitrile/toluene under nitrogen, with all volatiles removed under vacuum after the filtration of unreacted $IrH(dppe)_2$. Anal. of the crude isolate: C, 60.1; H, 4.74; N, 1.4. Calcd. for "$Ir(dppe)_2BF_4+C_6H_5NO_2$": C, 58.1; H, 4.46; N, 1.17. IR included absorption at 2060 cm^{-1} (νNN of $Ir(N_2)(dppe)_2BF_4$?).

Chapter IV

Biscyclopentadienyl Complexes of Molybdenum, Rhenium, and Tungsten with Diazo Ligands.

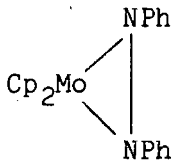
A. Introduction

The study of the reaction of diazonium salts with bis(cyclopentadienyl)metal hydrides arose from our desire to synthesize new aryldiazenido complexes with relatively simple coordination, more specifically, complexes having no phosphines. This prejudice formed because it seemed that most aryldiazenide complex chemistry involved phosphine complexes of low-valent metals (the most obvious exception being $CpM(CO)_2NNAr$[193]), and that some potentially interesting chemistry was thus being largely ignored. Attempts to prepare other phosphine-free aryldiazenido complexes are reported in later chapters.

The property of Cp_2MH_n, where M = Mo, W and Re, and n = 2 for the group VI metals and 1 for Re, which most interested us was its basicity. Each of these hydrides can be protonated by aqueous acid.[194] The molybdenum and tungsten complexes had been shown to reduce alkenes and alkynes, reacting via insertion into metal-hydrogen bonds.[196] With strongly electron-withdrawing substituents on the reactant hydrocarbons, the intermediate insertion products were impressively stable.

A few months after our investigations started, a paper appeared on the reactions of Cp_2MH_2 with diazo and diazene ('azo') compounds.[89] The diazo chemistry was generally uninteresting. Methyldiazoacetate was found not to react with Cp_2MoH_2 at room temperature; in refluxing thf it did so, but with loss of N_2. Cp_2WH_2 did not react even in refluxing thf. Similarly, diazomethane does not react with Cp_2ReH.[197] With diazofluorene at 353 K, Cp_2MoH_2 reacted to give Cp_2Mo(diazofluorene) and fluorene azine.[89]

The reactions reported with azo compounds were more encouraging.[89] Diazenes with electron-withdrawing ester substituents, $ROCON{=}NCO_2R$, reacted at room temperature with Cp_2MoH_2 to give 1,2-addition products, e.g. $[Cp_2MoH\{N(CO_2R){-}NHCO_2R\}]$ much like the activated hydrocarbons. In refluxing thf with excess diazene these decomposed to 1,2-disubstituted hydrazines and $Cp_2\overline{Mo{-}N(CO_2R){-}N{=}C(OR){-}O}$. The less-active diazene azobenzene reacted only at 343 K; at this temperature the presumed intermediate $Cp_2MoH(NPhNHPh)$ reacted with another molecule of azobenzene to give 1,2-diphenylhydrazine and



A single sentence in a communication[198] had reported isolation in low yield from Cp_2WH_2 and benzenediazonium tetrafluoroborate a compound formulated to be $[Cp_2WNNPh]BF_4$, having $\nu(NN)$ at about 1800

cm^{-1} in the infrared spectrum[199]. This compound has never been detected during the work reported herein.

Our first efforts were with Cp_2MoH_2. The stoichiometry of Cp_2MoH_2 to diazonium used was 1:1 until we obtained a solid 1:2 product directly from a reaction mixture. When the tungsten chemistry was started a stoichiometry of 1:2 was applied with no success. The work was shelved for over two years and only upon returning to it was a 1:1 reaction with Cp_2WH_2 attempted. This combination has been thoroughly successful and is presented first, followed by other tungsten, molybdenum, and rhenium results and a discussion.

B. Results

Reactions with all three metals have been done in a closed system to allow monitoring of any evolved gas. The various pressure changes observed indicated that less that 3% of added diazonium salt reacted with evolution of dinitrogen, dihydrogen, or other gas. Bubbling was noted only for reaction of solid 4-nitrobenzenediazonium salt with methanolic Cp_2WH_2 when mixed at room temperature. (Reactions were generally done at low temperatures. See Chapter IV,D.) With Cp_2MH_2 in molar excess of diazonium salt, the dihydride remained after reaction. Up to two moles diazonium salt were taken up by a mole of Cp_2MH_2, provided the reaction was not stopped short of completion. This occurred prominently for reactions in tetrahydrofuran in which the diazonium salt was very slow to react, presumably simply because it must dissolve first and does so only very slightly even at room temperature.

1. Synthesis and Spectroscopic Characterization of $[Cp_2WH(NNHAr)]^+$.

When a methanolic solution of diazonium ion was added to a toluene solution of Cp_2WH_2 below ca. 258 K, the mixture briefly (ca. 2 s) developed an orange color. This was similarly transient at 200 K in pure methanol and so the material responsible for solution color was not isolated. It may be simply a loose charge-transfer complex.[196b,c] During addition, or with removal of some solvents under vacuum near 253 K, amorphous, bright yellow solid 14 formed in suspension. It analyzed as a 1:1 adduct. (See Table IV-1 for listing of compounds and analyses.) There was a strong tendency either to oil or decompose upon attempted recrystallization, but a solid could be obtained from methanol/ether/hexane or propanone/hexane working quickly in cooled solution. Small, single crystals were grown at 263 or 195 K from propanone/toluene or propanone/hexane. These were initially bright yellow. Upon exposure to air, especially when warm (R.T.), the solid became distinctly green. Considering the sensitivity of Cp_2WH_2 to air, hydride 14 is surprisingly air-stable. A dry, solid sample was left out in air 10 h with only minor color change. The solid was not sensitive to light. Dry solids kept moderately well under nitrogen at room temperature. Heated in air, they decomposed below 373 K; no single temperature of melting or decomposition could be defined.

The solubility of 14 was typical for a monocationic complex tetrafluoroborate: very soluble in ethanenitrile, soluble in propanone,

Table IV-1. Elemental Analyses of Biscyclopentadienyl Complexes: $[Cp_2WH(NNHC_6H_4\text{-}4\text{-}G)]A$, 14; $[Cp_2W(NH_2NC_6H_4\text{-}4\text{-}G)]A$, 15; $[Cp_2Re(NHNC_6H_4\text{-}4\text{-}G)]A$, 22; and $Cp_2Re(NNC_6H_4\text{-}4\text{-}OMe)$, 23.

No.	G	A	Percent Composition					
			Found			Calculated		
			C	H	N	C	H	N
14a	H	BF_4	38.0	3.41	5.33	37.8	3.37	5.51
14b	OCH_3	BF_4	39.5	3.79	4.94	37.9	3.56	5.21
14c	CH_3	BF_4	Not analyzed					
14d	CH_3	PF_6	35.4	3.27	4.81	35.2	3.30	4.83
14e	F	PF_6	34.4	3.01	4.71	32.9	2.76	4.80
15a	H	BF_4	38.2	3.44	5.38	37.8	3.37	5.51
15b	OCH_3	BF_4	37.9	3.61	5.33	37.9	3.56	5.21
15c	CH_3	BF_4	38.9	3.85	5.26	39.1	3.67	5.37
15e	F	PF_6	38.8	3.31	4.34	38.7	3.36	4.32[a]
22b	OCH_3	BF_4	38.5	3.54	5.35	37.8	3.36	5.19
22e	F	PF_6	32.9	2.74	4.64	32.8	2.58	4.78
23	OCH_3	-	41.4	3.83	5.17	45.2	3.80	6.20

a) Calculated including 0.7 $C_6H_5CH_3$ in agreement with proton magnetic resonance intensities.

methanol; slightly soluble in CH_2Cl_2; insoluble in ether, toluene, hexane. Complex 14 was not stable in degassed solutions of dried solvents above ca. 258 K, isomerizing as described below. With addition of HBF_4 solutions turned brown immediately.

Nuclear magnetic resonance spectra of 14 (See Figure IV-1, and Table IV-2.) at different temperatures below 260 K, and of a ^{15}N(1) analogue, allow a full structural picture to be drawn. Appearance of a high-field PMR resonance, below δ -2, identifies 14 as a metal monohydride complex. This peak is relatively broad due to coupling with ten cyclopentadienyl hydrogens, not resolved for the hydride signal. It is the only peak in the spectrum which shifts appreciably with change of temperature, dropping from δ -2.09 at 259 K to -2.18 at 230 K (for 14d).

The aryldiazo group has a low-field resonance near δ 11 which does not split in 14c-^{15}N(1). Since with ^{14}N(1) this peak becomes sharper at low temperatures (5 Hz at 237 K vs. 7 Hz at 259 K), as expected with a decrease in broadening due to slow exchange, the proton is not decoupled from the ^{15}N dipole simply due to rapid exchange. It must be bound at N(2), giving a hydrazido(2-) complex, $[Cp_2WH(NNHAr)]^+$. The resonances of the 2,6- and 3,5-aryl hydrogens appear rather well separated and in 14d and 14e are interpretable in first order terms. (See Table IV-2.) Resonances of aryl substituents occur at typical frequencies.

Table IV-2. ^{1}H-NMR Data for Biscyclopentadienyl Complexes: $[Cp_2WH(NNHC_6H_4\text{-}4\text{-}G)]A$, 14; $[Cp_2W(NH_2NC_6H_4\text{-}4\text{-}G)]A$, 15.

No.		Anion	Position[a]	Description[b]	[Integ.]	Assignment
14a	H	BF_4	11.0	br s	[0.6]	N(2)H
	(254 K)		7.66-6.74	m	[5.]	phenyl
			6.13	br s FWHM=5 Hz	[10.]	Cp
			<0	not observed		
14d	CH_3	PF_6	10.8	br s FWHM=7 Hz	[1.]	N(2)H
	(259 K)[c]		7.19	d, J=8 Hz	[2.5]	3,5-aryl & PhMe
			6.73	d, J=8 Hz	[2.]	2,6-aryl
			6.05	d, J=0.6 Hz, FWHM<2 Hz	[10.]	Cp
			2.33	s	[3.]	Me
			-2.09	m, FWHM=3 Hz	[1.]	WH
14e	F	PF_6	10.8	br s FWHM=5 Hz	[0.9]	N(2)H
			7.07	pseudo t, $J_{FH}=J_{HH}=9$ Hz	[2.]	3,5-aryl
			6.77	d of d, $J_{HH}=9, J_{FH}=5$ Hz	[2.]	2,6-aryl
			6.04	br s FWHM=11 Hz	[10.]	Cp
			-2.05	m FWHM=3.5 Hz	[1.]	WH
15a	H	BF_4	7.28-6.61			phenyl & PhMe
			5.52	s		Cp
			3.96	br s FWHM=14 Hz		NH_2
			2.33	s		trace PhMe
			2.17	s		trace Me_2CO

Table IV-2 (continued). ^{1}H-NMR Data for Biscyclopentadienyl Complexes.

No.		Anion	Position[a]	Description[b]	[Integ.]	Assignment
15b	OCH_3	BF_4	6.79	pseudo d, J=9 Hz		3,5-aryl
			6.57	pseudo d, J=9 Hz	[4.0 total]	2,6-aryl
			5.49	s	[10.]	Cp
			3.92	br s FWHM=15 Hz	[1.7]	NH_2
			3.71	s	[3.0]	OCH_3
15c	CH_3	BF_4	7.21	s	[0.5]	PhMe
			7.04	pseudo d, J=8 Hz	[2.0]	3,5-aryl
			6.55	pseudo d, J=8 Hz	[2.0]	2,6-aryl
			5.50	s	[10.]	Cp
			3.92	br s[d] FWHM=14 Hz	[1.6]	NH_2
			2.32	s	[0.4]	PhMe
			2.22	s	[3.1]	Me
15d	CH_3 (267 K)	PF_6	6.98	pseudo d, J=8 Hz		3,5-aryl
			6.52	pseudo d, J=8 Hz	[4.0 total]	2,6-aryl
			5.49	s	[10.]	Cp
			3.93	br s[c] FWHM=8 Hz	[1.8]	NH_2
			2.20	s	[3.6]	Me
15e	F	PF_6	7.17	s	[3.5]	PhMe
			7.02-6.52	complex	[4.0]	aryl
			5.40	s	[10.]	Cp
			3.90	br s	[1.7]	NH_2
			2.32		[2.1]	PhMe

---

a) Reported in ppm downfield from internal tetramethylsilane.

b) Abbreviations: s, singlet; d, doublet; t, triplet; br, broad; FWHM, full width at half maximum.

c) See text for discussion of temperature dependence.

d) In ^{15}N(1) analogue: d, J=88 Hz, FWHM=2 Hz.

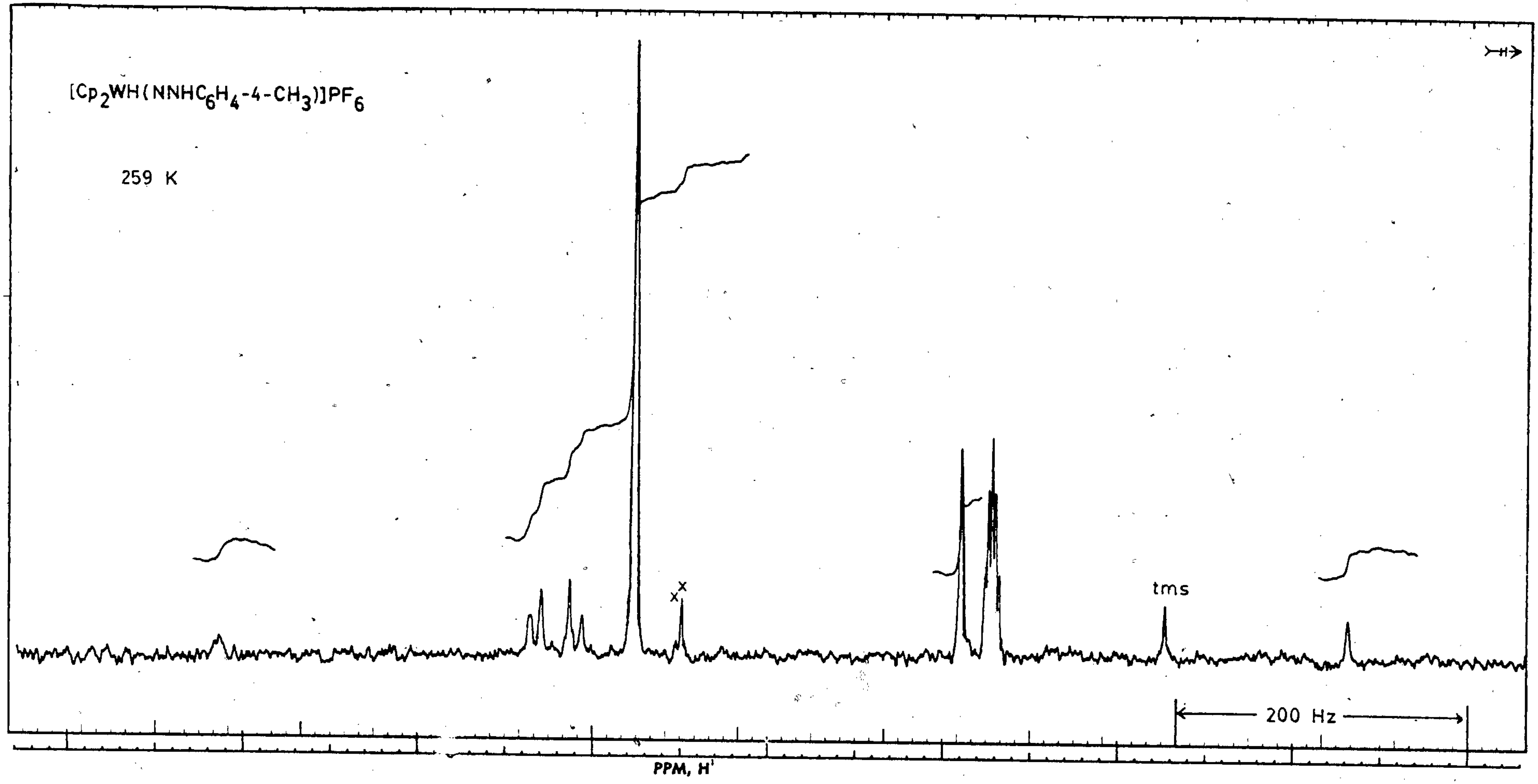


Figure IV-1a. 60MHz Proton Magnetic Resonance Spectrum of [$Cp_2WH(NNHC_6H_4\text{-}4\text{-}CH_3)$]$PF_6$ at 259 K. Peaks marked with X due to trace impurities including 15.

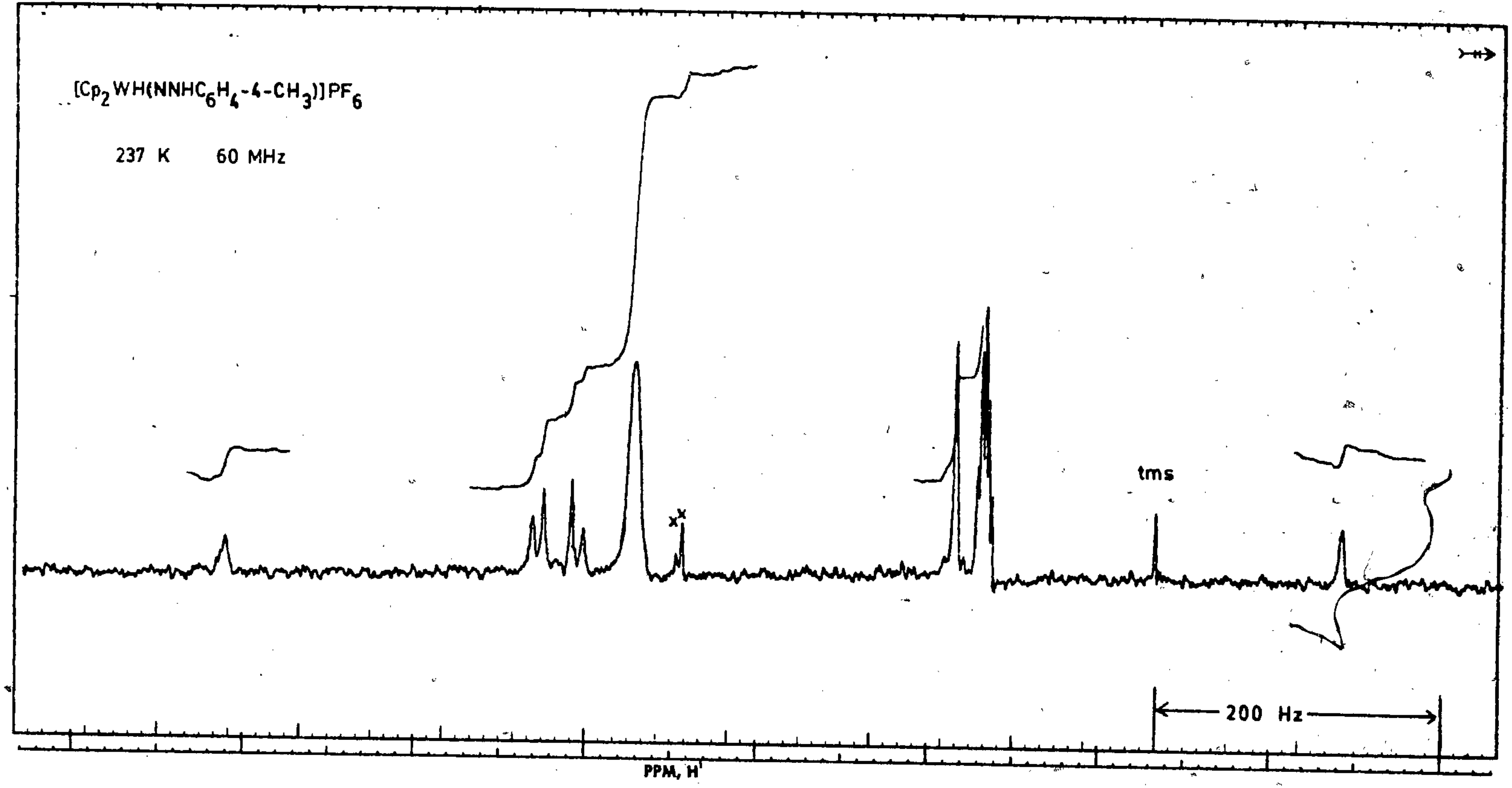
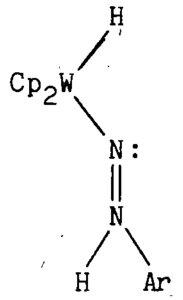


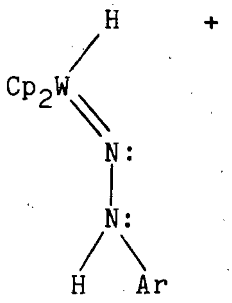
Figure IV-1b. 60 MHz Proton Magnetic Resonance Spectrum of $[Cp_2WH(NNHC_6H_4\text{-}4\text{-}CH_3)]PF_6$ at 237 K. Peaks marked with X due to trace impurities including 15.

What is the geometry of the hydrazido(2-) group? Crystallography has shown earlier examples with Group 6 and 7 metals to be linear at N(1).[141,147] In each of these examples the metals obtain an 18-electron configuration with this electron arrangement. (See Chapter II.) But $[Cp_2WH(=N=NHAr)]^+$ is a system with 20 valence electrons about the metal. There are two possible ways for this system to return to a more stable 18-electron configuration.[200] The first is exemplified by recent crystal structures of $Cp_2VNN(SiMe_3)_2$[201] and $Cp_2W(CO)_2$[202] in which one or both cyclopentadienyl rings bend to become a trihapto ligand. Note the first case in particular. The vanadium complex is formed from Cp_2V and $Me_3SiNNSiMe_3$, through an unstable intermediate which is probably a π-coordinated diazene.[203] This 17-electron complex rearranges to a "19-electron" complex which, like $Cp_2Mo(Me)(NO)$,[204] becomes assymetrically bound to the cyclopentadienyl rings. From this chemistry and that of the hydrazido complexes discussed in Chapter II, a clear tendency can be seen for N_2R_2 to bind to early transition metals as hydrazido(2-) species rather than as diazenes. (Wiberg calls these "isodiazene" complexes.[203] This nomenclature does describe the electronic structure better than "hydrazido(2-)" and is unambiguous when applied to the recently detected parent, H_2NN,[205] but its application to complexes is not advisable.)

The second possibility is that the diazo function could bend at N(1). There are two resonance forms which could be applied to such a structure, both with an 18-electron configuration at the metal.



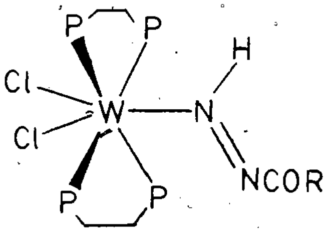
or



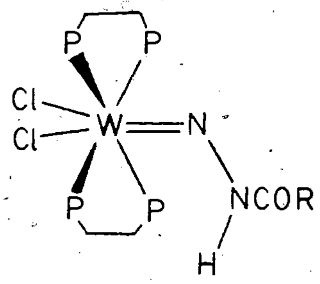
A

B

The possibility that the complexes WCl$_2$(NH=NCOR)(dppe)$_2$ might exist in solutions in an equilibrium mixture of structure B and an acyl- or aroyl-diazene form has been suggested.[39]

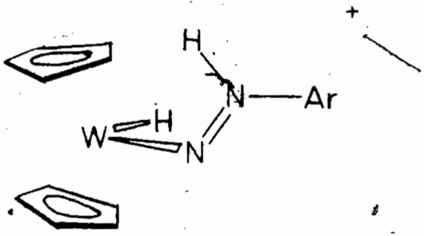


and



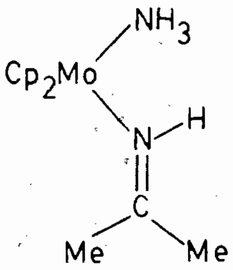
Of the options presented, structure A is the most consistent with the data. The NH chemical shift would seem to exclude both form B above and a linear W=N=NHAr structure since these are, respectively, expected to have or known to have amine-like rather than diazene-like chemical shifts. The infrared (vide infra) NN stretching frequency is high for an N-N single bond, also excluding form B.

The proton magnetic resonance due to the two cyclopentadienyl rings is also instructive. At higher temperature the sharp signal is a doublet (J= 0.6 Hz, combined width is 1.8 Hz at 259 K) due to coupling with the hydridic proton. As the temperature is lowered to 230 K the peak broadens dramatically to 10 Hz, though other resonances are not appreciably affected. Since the motion of the rings about the metal-ring center axis is not slowed at much lower temperatures in other complexes,[206] the broadness must arise from the slowing of a motion of the hydrazido(2-) ligand out of the midplane of the Cp_2WH to make the rings inequivalent, without changing the environment of the hydrazido(2-) protons or the metal-bound hydride. In other words the preferred dihedral angle between the Cp_2W midplane and the WNN plane is 90^o rather than 0^o.



14

It is novel that the diazo ligand should approach the ring this way. More normal modes of bonding are those exemplified by $Cp_2VNN(SiMe_3)_2$ in which the silicon and nitrogen atoms all lie in the midplane and V-N-N is linear,[201]



in which the imine lies in the midplane,[207] and

$[Cp_2WH(C_2H_3R)]^+$ in which the alkene is π-bound.[208] As observed in PMR, in the molybdenum complex the rings are equivalent at room temperature and would be expected to remain so at lower temperature. In the tungsten complex the rings are inequivalent even at room temperature, except where R=H, because of the interaction of R with only one cyclopentadienyl ring. Though these three examples offer no precedent for the structure of 14, the broadening effect seen with 14 is reminiscent of Cp_3MoNO in which the η^1-cyclopentadienyl freezes out below 190 K in a position which eclipses one or the other of the η^5-cyclopentadienyl rings, making them inequivalent.[206] We have not yet reached the expected limiting spectrum of two sharp signals, one for each cyclopentadienyl ring.

Complexes 14 have distinctive infrared spectra as well. (See Figure IV-2.) The W-H stretch expected near 1850 cm^{-1} cannot be seen in the infrared spectra. The change of dipole as the atoms vibrate is apparently negligible. This has been noted before for tungsten complexes.[209] There is a single, strong, sharp band near 3240 cm^{-1} (3270 cm^{-1} for PF_6 salts) due to NH stretching. The intensity of this band is higher than that of the diazenes with which we have experience. The expected 1,4-aryl and substituent absorptions are seen. Peaks assigned to cyclopentadienyl are found near 3120, 1500 and 1020 cm^{-1}. Positions of other expected Cp absorptions can not be definitely assigned; the bending mode occurs between 850 and 800 cm^{-1} where the bending mode of the 1,4-aryl group also absorbs, so one can

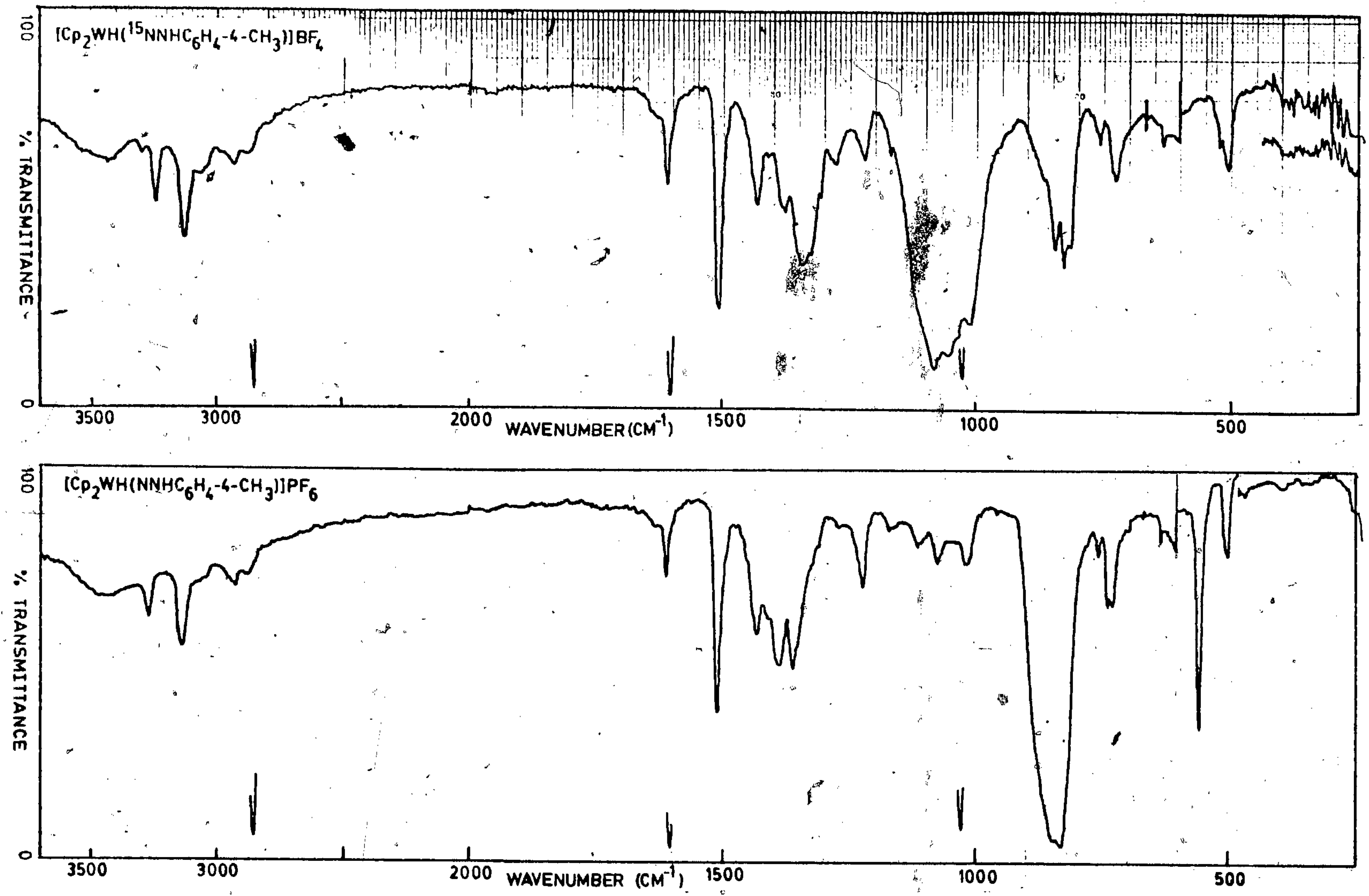


Figure IV-2. Infrared Spectra of [Cp$_2$WH(NNHC$_6$H$_4$-4-CH$_3$)]PF$_6$ and [Cp$_2$WH(^{15}NNHC$_6$H$_4$-4-CH$_3$)]BF$_4$.

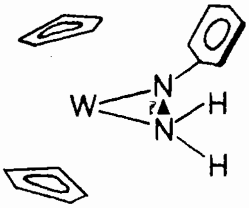
not confidently assign bands to the aryl or cyclopentadienyl ring. Furthermore even the phenyl derivative has two peaks in this region, possibly due to the bending mode of two cyclopentadienyl rings separated by the different interaction with the hydrazido(2-) ligand. Upon substitution with ^{15}N at N(1), a band at 1360 cm^{-1} shifts to become a broad peak centered near 1340 cm^{-1}. On this basis we assign the 1360 cm^{-1} peak as ν NN. This is well below the energy of this vibration in other coordinated diazenes,[122] but still indicative of a degree of multiple bonding between the nitrogens.

2. Synthesis and Spectroscopic Characterization of $[Cp_2W(NH_2NAr)]^+$.

The addition of methanolic $4\text{-}CH_3C_6H_4N_2BF_4$ to Cp_2WH_2 in toluene was done at 273 K and a brown product, 15, obtained directly in high yield. Analyses indicated that 15 was an isomer of 14. (See Table IV-1.) Analogues of this compound with other substituents on the benzene ring were obtained by letting solutions of 14 stand for at least 1 h between 273 K and room temperature. In shorter periods, especially at lower temperatures, the conversion of 14 to 15 was incomplete. Solid 15 could be recrystallized from propanone/toluene. Filtration of the propanone solution before recrystallization removed flocculent insoluble solids of two types: brown 16 was slightly soluble in ethanenitrile and had ν NH at 3340 cm^{-1}; black 17 was insoluble in all solvents and had no infrared bands useful for characterization.

The proton magnetic resonance spectra of 15 (See Table IV-2 and Figure IV-3.) showed, at δ 3.9, broad absorption integrating to two protons which disappeared with addition of D_2O and split with $^{15}N(1)$ substitution ($^{1}J_{(^{15}NH)}$=88 Hz). The resonance is assigned as two equivalent nitrogen-bound hydrogens. It is quite unusual to see protons of coordinated hydrazine in an NMR spectrum,[210] so such a coupling has not been seen before. The slow exchange necessary for the coupling implies that N(1) has no lone pair promoting ready proton transfer,[211] that N(1) is metal-bound.

There was a sharp singlet corresponding to all ten Cp protons, shifted upfield from the frequency in 14. If the structure suggested,



15

were static then the two cyclopentadienyl rings (and the nitrogens) would be affected differently by the aryl ring and would split, but inversion of pyramidal nitrogen would average out the effect on an NMR time scale. The chelation of this arylhydrazide is similar to that in the phenylhydrazine complex [CpMoI(NO)(NH_2NHPh)]BF_4.[88]

The phenyl protons of 15a gave a complex pattern but 15b, c, and e were interpretable in first-order terms. The 2,6-protons resonate upfield of the 3,5-protons and all resonances were shifted upfield from their positions in the corresponding 14 complex. Chemical shifts of

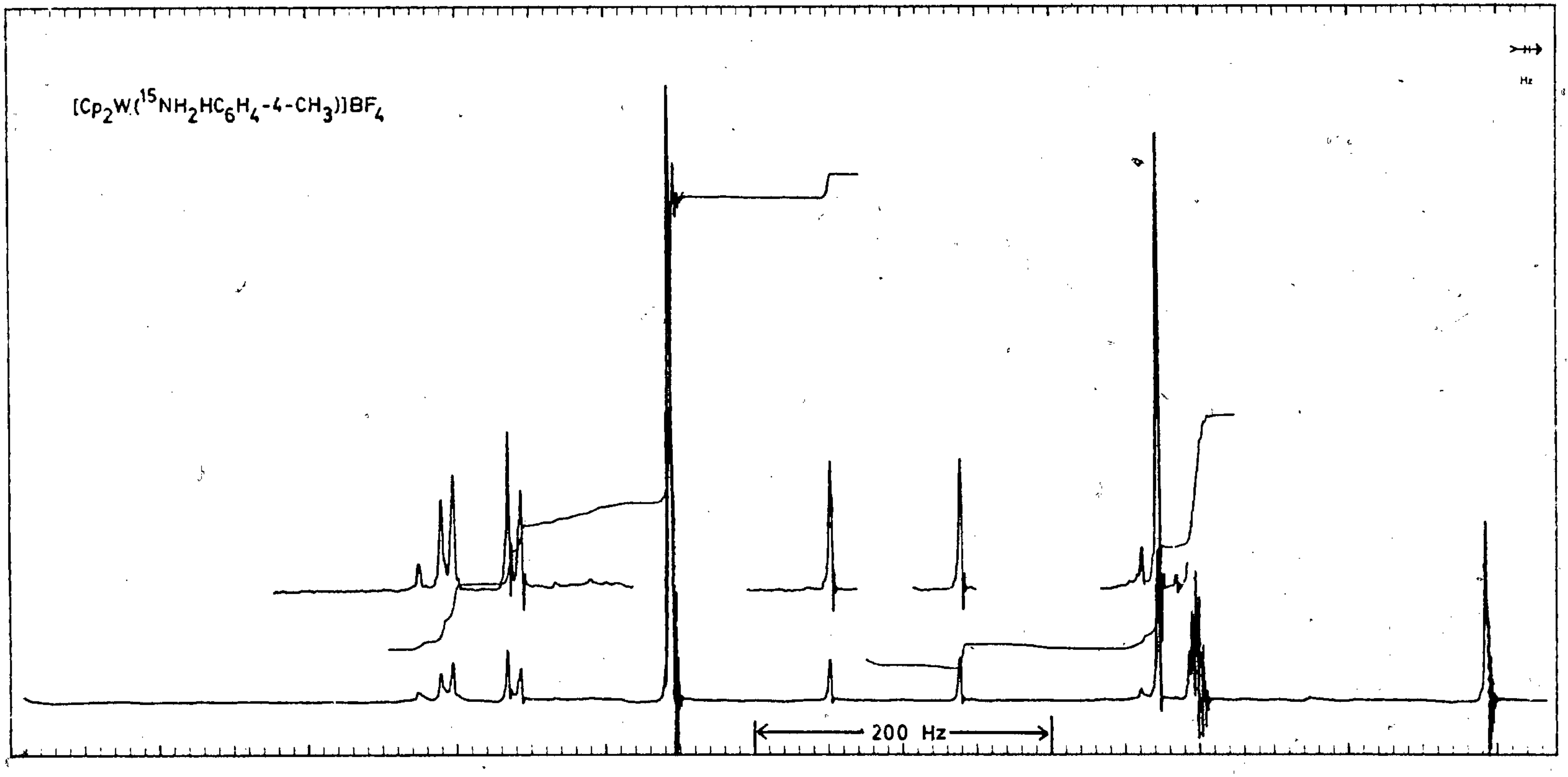


Figure IV-3. 100 MHz Proton Magnetic Resonance Spectrum of $[Cp_2W(^{15}NH_2NC_6H_4\text{-}4\text{-}CH_3)]BF_4$.

protons often are interpretable in terms of electron density arguments, but the relative upfield shifts of cyclopentadienyl and aryl protons in 15 can not both be explained in this way. Rather, the aryl shift is probably the one corresponding to a real electron density increase. The Cp signal of complexes 14 might be shifted downfield because of the magnetic anisotropy of the diazo group which, since it is out of the midplane, approaches the cyclopentadienyl rings closely; conversely the Cp signal of 15 might be shifted upfield because of the magnetic anisotropy of the aryl ring.

Infrared spectra of 15 were rather simple. (See Figure IV-4.) The NH_2 group had two strong bands as expected, due to asymmetric and symmetric stretching at 3300 and 3240 cm^{-1} (3340 and 3260 cm^{-1} for PF_6 salts). The NH_2 bend occurred close to 1610 cm^{-1}, with aryl intensity superimposed. With ^{15}N-substitution at N(1), the NH_2 nitrogen, no band in the region 1600-800 shifted significantly so νNN could not be identified. The shift of a weak band at 448 cm^{-1} was significant, though barely so. Assignment to ν W-N(1) or a mode involving this motion is not reasonable since a band occurs here in 14b and 21 as well.

A relatively intense band appeared near 1325 cm^{-1}, not present in 14 and so characteristic of the new mode of coordination. This is tentatively assigned to νN(2)-C(aryl) since a band is commonly found in this region with aryl amines, at somewhat high frequency for a single

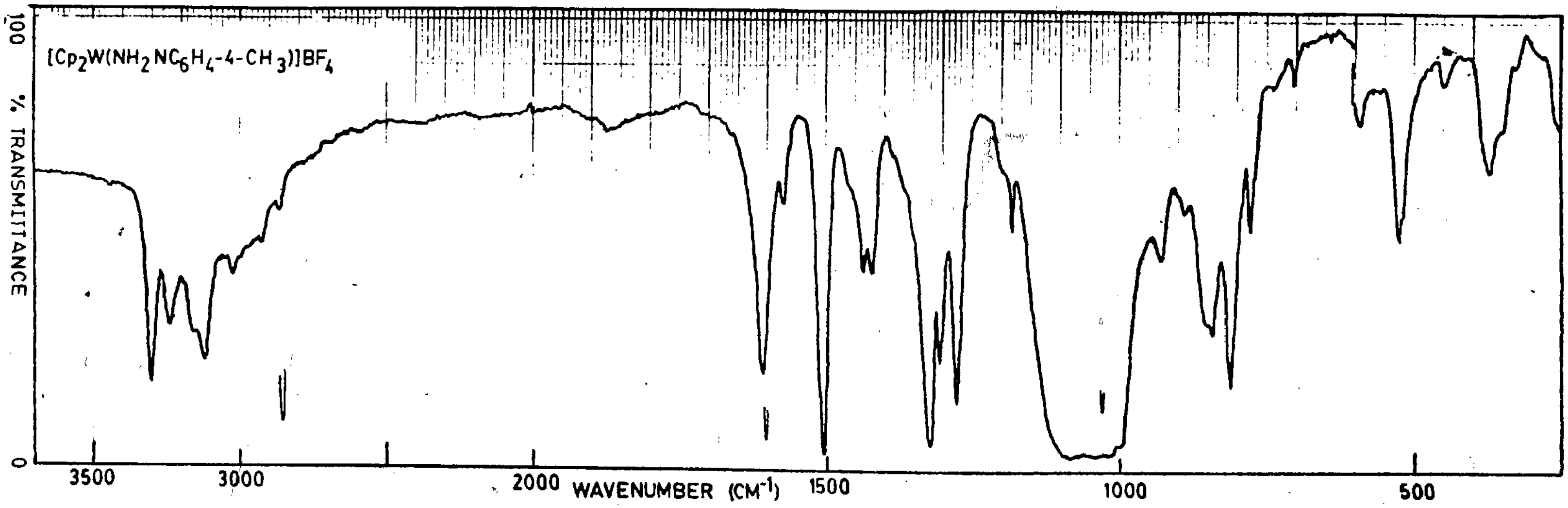
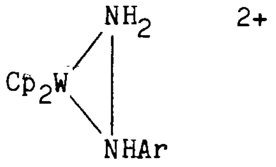


Figure IV-4. Infrared Spectrum of [$Cp_2W(NH_2C_6H_4\text{-}4\text{-}CH_3)$]$BF_4$.

bond due to partial C–N multiple bond character with delocalization of the lone pair onto the ring.[212] This same conjugation is presumably the mechanism of the increased magnetic shielding of aryl protons in 15 compared to 14. (vide supra) No other peaks appear exceptional.

3. Other Cp_2W-Containing Products.

In one trial a purple solid, 18, was successfully prepared by addition of a dilute HBF_4 solution in methanol to 15c and evaporation of methanol under vacuum. It could be recrystallized from propanone/ether. The NH stretching frequencies in this occurred at about 3340, 3295(sh), and 3220 cm^{-1}, and an NH_2 bend at 1635 cm^{-1}. We tentatively assign the structure



to the complex cation. The C,H,N analysis was done after ether trituration but before recrystallization and so the sample was contaminated with HBF_4.

When one mole of Cp_2WH_2 was combined with two moles of diazonium tetrafluoroborate in methanol at 200 K no reaction was apparent. Upon warming to room temperature the solution became red-brown and then dark chocolate brown. A crude residue left after removal of all volatiles analyzed close to the values expected for the combination of reactants in a ratio of 1:2 hydride to diazonium. An infrared showed absorption typical of NH, π-cyclopentadienyl and aryl. Attempted purification by precipitation from methanol of the redissolved crude product led to isolation of a black solid which had the same proportion of C and N but which was quite low in both. This was no longer methanol-soluble and may be 17. The brown filtrate when dried had an odor reminiscent of a high alkane, suggesting some free cyclopentadiene-derived product. It appeared that further work with 1:2 reactions of this tungsten hydride would not be at all productive.

4. Reactions of Cp_2MoH_2

Reactions of Cp_2MoH_2 have all been done in a single solvent, generally methanol. The progress of reactions was obviously different from those with tungsten hydride since a permanent red or brown color developed even when addition was done in a dry-ice bath. When only one mole of 4-fluorobenzenediazonium tetrafluoroborate was added per mole molybdenum, a product, 19, analogous to 15 was produced, as indicated by infrared absorption of the crude, dried isolates, e.g. at 3300 and 3240 cm^{-1} (3330 and 3250 for PF_6^- salts). This was never successfully brought out of solution, even as an oil, unless solvent was nearly completely removed by evacuation. Thus it was never purified. To the extent that we could detect them in mixtures, the properties of 19 were close to those of tungsten complexes 15. The instability of 19 with respect to 20, the molybdenum analogue of 16, is greater. One sample, kept only in the dry box, completly decomposed to 20 over long (> 2 yr) storage. Degassing does not seem to hinder the rapid (< 1 hr) decomposition of 19 to 20 in solutions of alcohol, propanone or ethanenitrile at ambient temperatures. Because this instability was interpreted as extreme air-sensitivity, we did not try the low-temperature preparation of nmr solutions without which the spectra were grossly complicated with decomposition products. On the basis of our results with the tungsten complex 16, conducting work-up and taking solution spectra at low spectra at low temperatures (< 273 K) should allow useful investigation of 19.

The reaction of Cp_2MoH_2 with two moles of diazonium salt added quickly produced a purple-red, methanol-insoluble product, 21, which analyzed as a 1:2 adduct, $[Cp_2MoH_2 \cdot 2\ NNC_6H_4OMe](BF_4)_2$. The same substance was also isolated in the reaction of equimolar amounts of Cp_2MoH_2 and 4-methoxybenzenediazonium tetrafluoroborate. The expected product, 19, was present in the filtrate of 21 in this case. The low solubility of 21 in solvents other than ethanenitrile and propanone was in agreement with formulation as a 1:2 electrolyte. The solid decomposed without melting above about 398 K. Degassed solutions were somewhat stable at room temperature, but decomposed completely over two weeks. Solutions lost redness rapidly upon exposure to air. Peaks in its infrared spectrum included the expected CH, $ArOCH_3$, and BF_4 stretches, the CH bend of a 1,4-disubstituted benzene, and other strong peaks useful for identification. A solution of 21 in a sealed tube was studied by proton magnetic resonance. There was no sign of a low field NH or high field MoH signal, but there were multiple peaks in positions

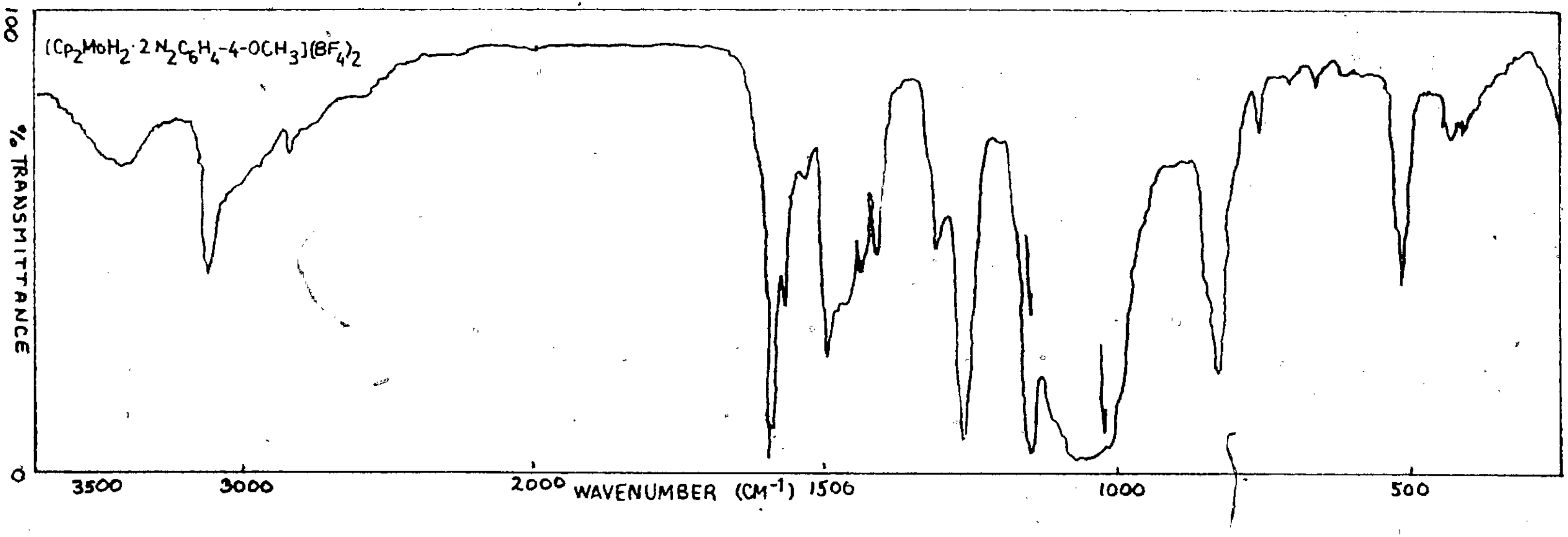


Figure IV-5. Infrared Spectrum of $[Cp_2Mo(NHNC_6H_4\text{-}4\text{-}OCH_3)_2](BF_4)_2$.

expected for Cp and OMe resonances, indicating a mixture of several substances was present. Changes occurred in the spectrum over a period of 12 days, with most peaks gradually losing intensity. Since the composition of the mixture of the initial spectrum was unknown, we could not determine what changes might be occurring.

The methanol-insoluble product 21 reacted with triethylamine in benzene, in which the unneutralized ionic complex is insoluble. The intensely colored benzene solution was separated by decanting and dried. The infrared spectrum of this duplicates that of the unneutralized material except in having vastly reduced intensities near 1050 and 520 cm^{-1}, both due to BF_4^-, and some weak absorptions due to Et_3NH. In spite of absence of N-bound H signals in infrared or nmr spectra, the facile neutralization suggests that the complex is a bisdiazene, for other acidic protons are more likely to have been infrared active.

5. Reactions of Cp_2ReH

Like the isoelectronic group VI hydrides, Cp_2ReH reacts at low temperatures in methanol with one mole of aryldiazonium tetrafluoroborate. No product separated from cold solutions so the reaction mixtures were allowed to warm to room temperature while solvent was removed under vacuum. The dark brown product, 22 was recrystallized at room temperature from propanone/ether or ethanenitrile/ether. Analysis indicated a 1:1 adduct, but the samples contained some decomposition products since C, H, and N analyses were generally low.

The solubility of **22** was characteristic of an ionic complex: soluble in ethanenitrile, propanone, methanol; insoluble in aromatic solvents, ether, hexane.

The spectral data are consistent with a formulation as $[Cp_2Re(NH{=}NAr)]^+BF_4^-$. The infrared spectra of **22** have a single NH stretch at about 40 cm^{-1} lower energy than the single band in tungsten complexes **14** with the same substitution. There is a strong, somewhat broad band near 1335 cm^{-1} which can not confidently be assigned, but which may be νNN. Otherwise the spectrum shows only the expected cyclopentadienyl, 4-methoxyaryl, and tetrafluoroborate bands. The PMR at ambient temperature had a very broad (ca. 15 Hz) signal at low field, consistent with a proton bound to a highly anisotropic nitrogen. Aryl resonances are at lower field than with the tungsten products **14** and **15**, suggesting less delocalization of electron density onto the ring in **22**. The cyclopentadienyl and methoxy singlets occurred as expected and are not useful in structural assignment. In sum, the spectroscopic data for the two derivatives at hand lead one to conclude that the rhenium complexes **22** are sufficiently different from **14** that the two have different atomic arrangements; that the rhenium complexes are aryldiazenes.

The complexes **22** are readily neutralized by CO_3^{2-} or Et_3N. The brown product **23** was identified as $Cp_2ReNNC_6H_4$-4-OMe by analysis and infrared, which showed no BF_4^-, no νNH, and no band at

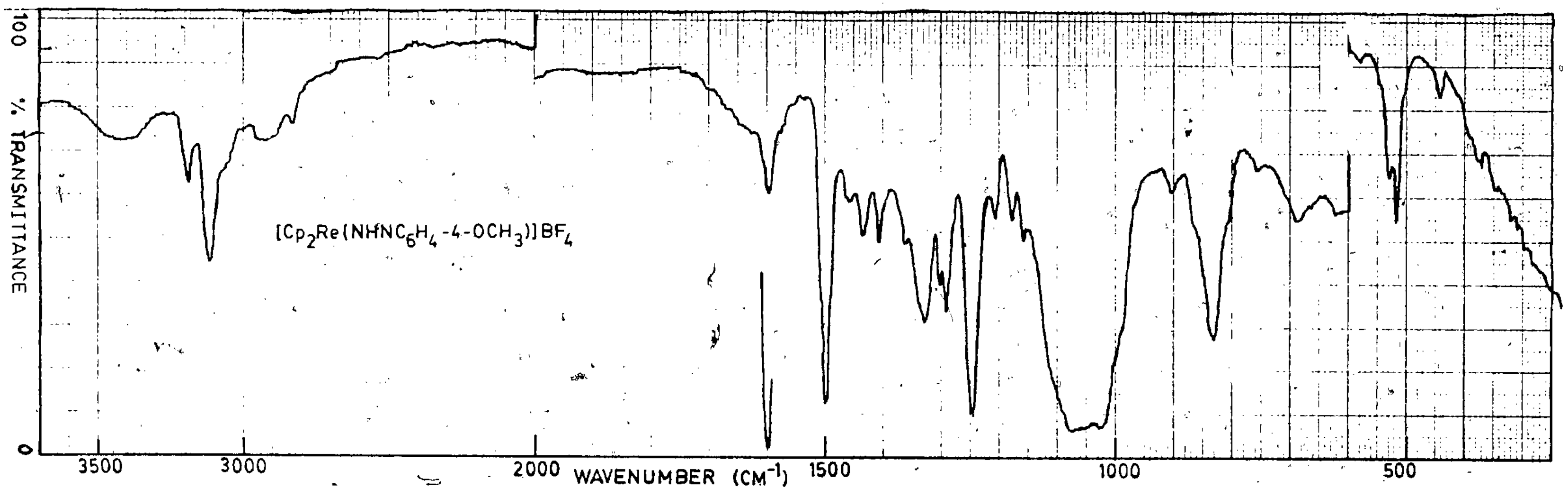
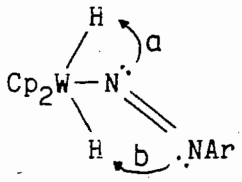


Figure IV-6. Infrared Spectrum of [Cp$_2$Re(NHNC$_6$H$_4$-4-OCH$_3$)]BF$_4$

all near 1335 cm^{-1}. A new, strong band at 1610 cm^{-1} is assigned as ν NN, undoubtedly coupled to aryl modes which show increased intensity at 1580 cm^{-1}.

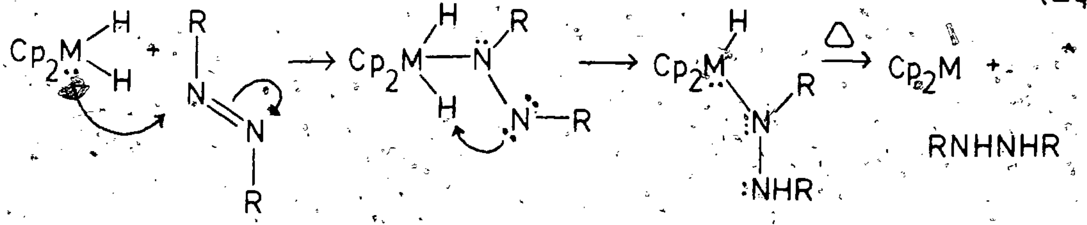
C. Discussion

It is likely that the first step in these reactions of Cp_2MH_n with diazonium salts is the formation of a metal-N(1) bond by electrophilic attack of diazonium on a metal lone pair. This would parallel the formation of complexes by Cp_2MH_n with Lewis acids, including H^+.[194] But when hydridometal complexes react with aryldiazonium salts, the insertion of the diazo group into the M-H bond of the resulting cation has always been so facile that the intermediate cationic diazenidohydridometal complex has not been detected. Since attachment to a cation withdraws electrons from the metal, the hydride bond loses electrons and the proton becomes more acidic. It is sensible that it might shift to a nitrogen, made basic upon coordination. Such a shift could initially be to either nitrogen,

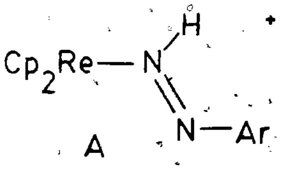


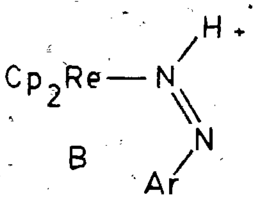
there being no apparent steric or symmetry restriction. Since a further proton shift between the nitrogens would probably also be fast, the thermodynamic product is expected rather than a purely kinetic one. This product has always been identified as the aryldiazene, but the mechanism need not be a 1,2-proton shift (a). In fact we suggest that aryldiazonium salts and 1,2-disubstituted diazenes with strongly electron-withdrawing substituents could react by a common mechanism: i) electrophilic attack by the diazo reactant, and ii) a 1,3-proton shift (b); when the product is an arylhydrazido(2-) ligand, this rearranges to the observed aryldiazene, but when the product is a hydrazido(1-) ligand no further change occurs. (See also equation IV-2.)

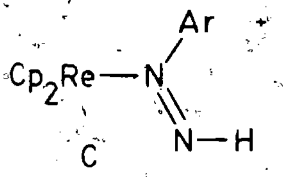
(Eq. IV-1)

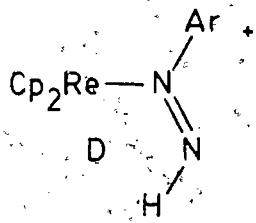


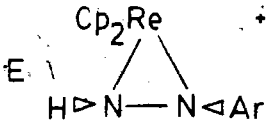
Though infrared and PMR allowed tentative characterization of the rhenium product 22 as a diazene rather than a hydrazido(2-) complex, there remains a rather large number of possible structures because the diazene could be either cis or trans, and the electron pair donated to the metal could be the lone pair at the aryl- or hydrogen-bound nitrogen or the π-electrons.

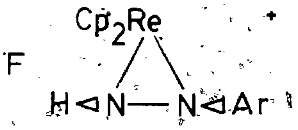












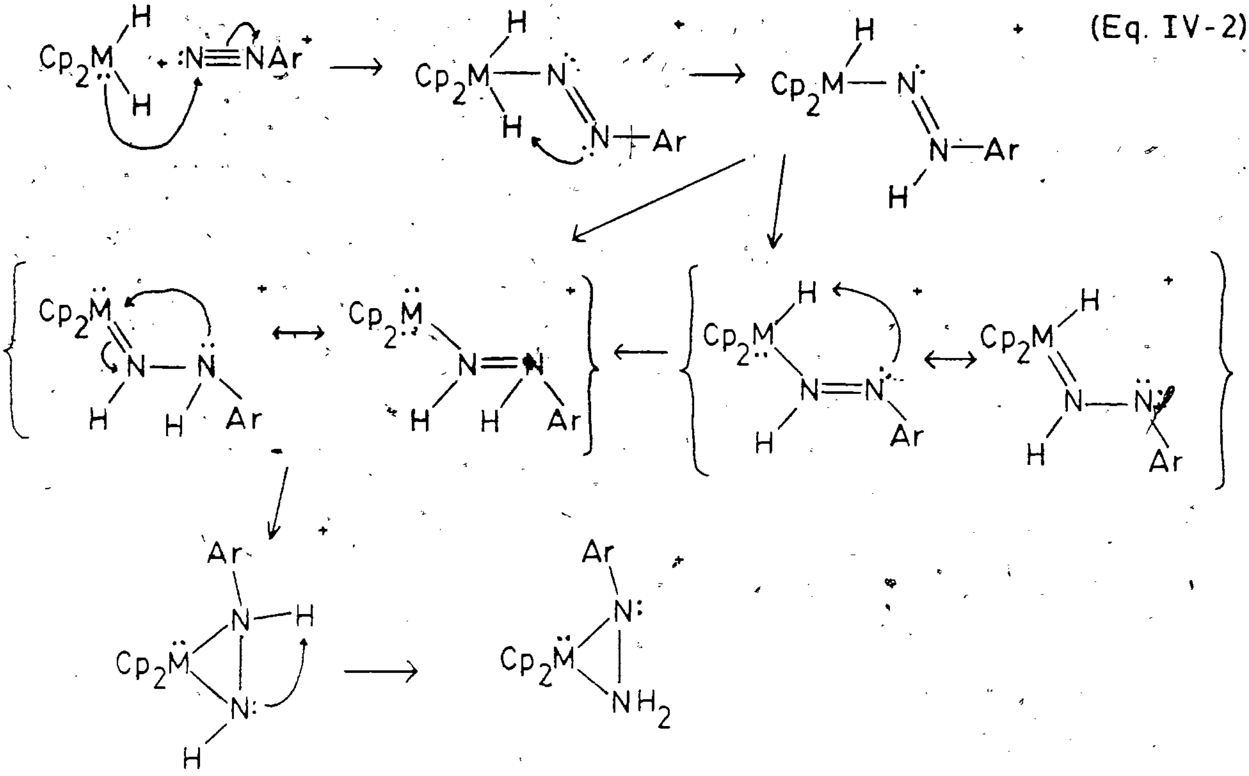
On the basis of precedent, structure A is most likely. Crystal structures of diazenes have shown them to be coordinated at the non-substituted nitrogen, with cis configuration (substituent trans to the metal), except when orthometalation necessitates a trans configuration. But there is no spectroscopic indication that excludes B. Structures C and D are less likely because they offer distinctly less possibility for electron delocalization, and are inconsistent with the acidity of 22. Further, the presence of a lone pair on the aryl-bound nitrogen is suggested by the equivalence or near-equivalence of the chemical shifts of the 2,6- and 3,5-aryl protons with 4-F and 4-CH_3O substitution, since a lone pair would allow comparable resonance forms to be drawn with electron density added to all four unsubstituted aryl carbons. The chemical shift of the N(1)-H eliminates structures E and F which would not have the necessary nitrogen anisotropy.[208]

The rhenium complexes require more study. The proton nmr spectra have never been free of minor resonances that may be due to impurities, some neutral [$Cp_2Re(NNAr)$] formed in solution, a structural isomer such as B, or the hydrazido(2-) form. It is possible that changes in aryl substitution could be meaningfully correlated with changes in pK_a or isomer equilibrium.

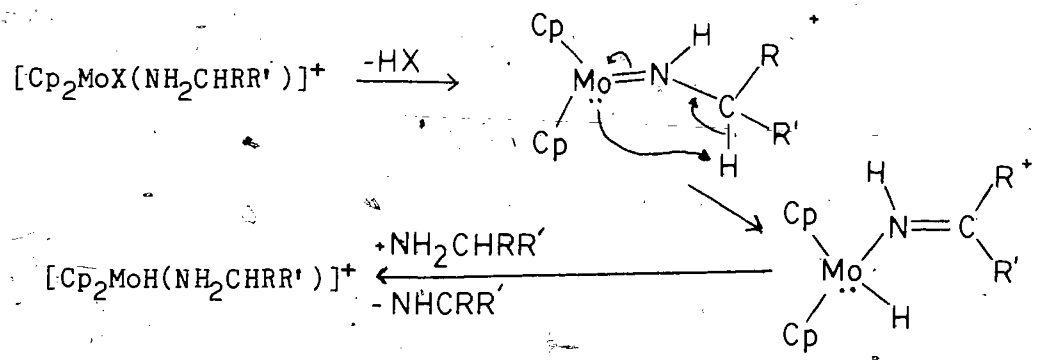
The mechanism of formation of tungsten complex 14 was given above. (See also Equation IV-2.) That it is formed is not surprising; that it, rather than the diazene, is isolated is: The implication is that the N(2) lone pair is more basic than the lone pair of the metal-bound nitrogen, N(1). It is not apparent why this particular compound should be subject to an inversion of nitrogen basicities. Two rationalizations seem plausible: (1) The lone pair at N(1) is slightly involved in binding to the metal. (2) Conjugation of the midplane lone pair on tungsten[213] with the diazenido N=N π-bond places additional electron density at N(2). (This conjugation could also be the basis for the tendency of the diazo group to bend out of the Cp_2W midplane rather than in it.) If the second rationalization is true, then other examples of the doubly bent hydrazido(2-) ligand should be found in complexes with very electron-rich metal centers.

An obvious question is how 14 isomerizes to 15. The evidence collected does not bear on the question, so an answer is in the nature of a rationalization. A possible mechanism is given as Equation IV-2.

(Eq. IV-2)



The several steps in formation of 15 are rather obvious once the structures of 14 and 15 are identified. No single step is particularly novel: the proton shift from the metal to diazene is the reverse of that postulated[207] in the reaction:



But the whole process certainly is interesting for it may bear on the inability of nitrogenase to reduce hydrazine. The dinitrogen complexes of transition metals are either linear monomeric or bridging. This has led discussion of biological mechanisms of N_2-fixation away from π-bound nitrogen intermediates, and somewhat toward bimetallic diazo-bridged intermediates. Complex 15 is related to π-bound intermediates, it is a chelating diazo ligand of bite size two. The bidentate ligand was formed from rearrangement of a singly coordinated diazo ligand. It is quite possible that hydrazine is not acted upon by nitrogenase because both nitrogens must be coordinated to allow reduction, but there is no pathway by which the the enzyme active site can coordinate both nitrogens, except by starting from a more oxidized form of diazo ligand.

The instability of 14, 15 and their molybdenum analogues is quite promising if such species are to be included in a model for dinitrogen fixation, for models of very reactive intermediates should also be reactive. Elemental analysis of the products of further decomposition of 14 and 15 appear to arise from gross changes of structure.

1:1 Reactions of the molybdenum hydride Cp_2MoH_2 with diazonium ions appear somewhat different from those of tungsten, but we feel the difference is not fundamental. We suggest the cause for much of the difference is simply the greater tendency of the molybdenum analogues of 14 and 15 to react further. For instance, while reaction mixtures of Cp_2WH_2 kept below ca. 258 K remain lightly colored, solutions of Cp_2MoH_2 become deep brown even at 200 K. The low-temperature color could be due to $[Cp_2Mo(NH_2NAr)]^+$, or to $[Cp_2MoH(NHNAr)]^+$ if this were colored like the rhenium diazene.

The inconsistencies and complexities of 1:2 adducts of each of the bis(cyclopentadienyl)hydridometal complexes with diazonium salts makes it difficult to anwer even basic questions. 1) What is the nature of 21? 2) Why does 21 form even with only 1:1 stoichiometry of the reactants present? 3) Why is the product of Cp_2WH_2 reaction with two moles diazonium salt different from 21? The second and third can not be discussed definitively until the first is answered and it presently seems that the first can not be answered without better separation of the product mixture. If the complexity in the proton NMR spectra of 21 is due to the presence of several of the ten geometric isomers of a bisdiazene complex (Each diazene could be cis or trans and oriented endo or exo.) then the problem may never be solved.

On the second point one can say that diazonium salt reacts rather easily with an intermediate which exists at 200 K. At this temperature Cp_2MoH_2 was not completely dissolved in the volume of alcohol used. The existence of 1:2 product from 1:1 stoichiometry could be due to reaction of dissolved diazonium salt in excess of dissolved Cp_2MoH_2 with dissolved intermediate. This would be especially significant in reactions a) under conditions where diazonium salt is much more soluble in the alcohol than Cp_2MoH_2, or b) where solid diazonium salt is added quickly or in larger portions.

This leads to the third point. Though the 1:2 molybdenum product is probably formed at 200 K, from solution color one can say that the tungsten 1:2 products clearly are not. At the higher temperature of reaction of the tungsten hydride with two moles diazonium salt, a greater variety of reactions might be feasible. The isolate from Cp_2WH_2 reactions using a 1:2 stoichiometry does indeed appear a mess, probably containing several products each in low quantity.

With establishment of the nature of 1:1 products, it would probably be fruitful to react these substances with a further mole of diazonium salt to see if this allows the synthesis of a single isolable product.

D. Experimental

1. Instrumentation, Techniques, and Reagents.

For general spectroscopic and experimental methods see Section III D 1,2. Low temperatures of PMR spectra were held automatically with a Varian V-6040 variable temperature controller. Temperature calibration was done by measuring the CH_3-OH chemical shift difference on a methanol sample run with the same temperature setting.[214]

Reactions of Cp_2MoH_2 and Cp_2ReH were done on a standard vacuum rack with solvents condensed onto the hydride at liquid nitrogen temperature. After melting the solvent, the solid diazonium salt was added by tipping a bent tube attached to one neck of the reaction flask. The tungsten reactions were done using the bench-top vacuum rack noted above.

$MoCl_5$, WCl_6, and $ReCl_5$ were obtained commercially (Alfa Products) and used as received. The hydrides were prepared according to a literature method.[215]

2. Reactions of Cp_2WH_2.

a. Cp_2WH_2 Reactions with Benzenediazonium Ion. Dropwise addition over 0.8 h of a solution of benzenediazonium tetrafluoroborate (119 mg, 0162 mmole) in methanol (18 ml) to a stirred, cooled ($253<T<265$ K) solution of Cp_2WH_2 (196 mg, 0.62 mmole) in 16 ml toluene under N_2 gave a color change to brownish yellow. Yellow solid 14a formed and collected on the walls of the flask underneath the solution surface. The mixture was evaporated under vacuum to less than half volume without noticeable change to the quantity of solid and then filtered. The filtrate was stripped to dryness, leaving a brown residue. An infrared of the brown residue indicated it to be 15a, but attempted crystallization from propanone/toluene cooled to 265 K gave a brown precipitate of 16a. Anal. Found: C, 24.8; H, 2.80; N, 3.15. Calcd. for "$C_{16}H_{21}N_2WB_4F_{16}$" C, 24.9; H, 2.74; N, 3.63. IR 3340 m, 3125 m, 1595 wm, 1488 wm, 1433 m, 1320 w, 1280 w, 1080-1050-1020 vs, 848 m, 750 wm, 694 w, 528, 518 cm^{-1} w. The filtrate of 16a upon standing in the freezer slowly deposited black 17a. Anal. Found: C, 26.2; H, 2.70; N, 2.34. IR had no νNH, and only a shoulder at 1600 cm^{-1}.

The yellow solid 14a was rapidly recrystallized from methanol/CH_2Cl_2/ether/hexane, filtered in air, washed with ether, and briefly air dried. (See Table IV-1 for analysis.) IR: 3240 s (νNH), 3131s (νCH), 1601 s, 1513 wm, 1496 s, 1441, 1430 s, 1405, 1384 s, 1358 s (νNN), 1283 m, 1218 m, 1173 m, 1155 m, 1090-1060-1018-1000 vs, 879 m, 852 s, 839 s, 753 s, 739 s, 690 s, 642 wm, 615 wm, 569 m, 525 m, 508 m, 375 cm^{-1} wm. (See Table IV-2 for PMR.) It decomposed in a vial nominally under N_2 in the refrigerator, turning distinctly olive green. In air on a hot stage, rapid decomposition did not occur below 363 K.

Solutions of 14a isomerized, when not well cooled, to 15a. This brown solid was recrystallized from propanone/toluene. IR: 3304 m, 3244 m (ν NH$_2$), 3124 s (ν CH), 1595 vs, 1486 vs, 1452 wm, 1436 wm, 1420 m, 1324 s, 1281 s, 1179 wm, 1085-1050-1020-995 vs, 845 s, 752 s, 694 m, 522 m, 451 w, 386 wm, 346 cm^{-1} wm.

2b. Cp_2WH_2 Reactions with 4-Fluorobenzenediazonium Ion.

In a similar reaction of 4-$FC_6H_4N_2PF_6$ (76 mg, 0.28 mmole) and Cp_2WH_2 (91 mg, 0.29 mmole) at 248<T<258 K, 14e was collected by evaporating the reaction mixture under vacuum for 0.3 h, cooling to 225 K, and filtering. The yellow solid 14e was allowed to drain well, then vacuum-dried; 53% yield. Its infrared spectrum clearly showed peaks due to toluene. It was recrystallized from methanol/ether/hexane but so much methanol was used that the recovery was poor. (See Table IV-1 for analysis.) IR: 3276 wm (ν NH), 3135 m (ν CH), 1625 vw br, 1507 vvs, 1431 m, 1411 m, 1392 s, 1361 m, 1205 s, 1151 wm, 1095 wm, 1072 w, 1020, 1008 wm, 833 vvs, 740 m, 559 s, 520, 504 m, 420 w, 357 cm^{-1} w. Small crystals were formed from propanone/toluene cooled in a capped tube under N_2 placed in an evacuated tube cooled to 195 K. Slightly larger crystals formed from slow diffusion of a hexane layer into a propanone/toluene/ether solution at 265 K.

The filtrate of the reaction mixture after removing 14e was partially stripped and allowed to stand at 265 K. The propanone-insoluble black solid which did collect was removed by filtration. The filtrate was stripped to dryness and purified by dissolving in a minimum of propanone (<0.3 ml) and precipitating with excess toluene. This gave a dark oil and some light brown solid which was filtered from the decanted solution. The treatment was repeated twice with the remaining oil to solidify all the residue. It was combined with the filtrate of the recrystallization of 14e and crystallized from 0.8 ml propanone/6 ml toluene, with slow cooling provided by placing the solution under N_2 atmosphere in a capped tube placed in an evacuated tube in dry ice. The cold solution was decanted from the fine brown crystalline needles which formed and the solid washed once with toluene and vacuum dried to a light brown solid. The analyses and PMR spectrum (Tables IV-1,2) both indicated 0.7 mole toluene, though it was not apparent from the infrared spectrum: 3336 m, 3261 wm (νNH_2); 3130 wm (νCH); 1605 wm, 1498 vs, 1421 wm, 1328 m, 1281 m, 1211 s, 1155 wm, 1106 wm, 1077 wm, 1014 wm, 993 wm, 918 m, ca. 845 vvs, 792 s, 739 m, 699 w, 559 s, 511 w, 470 cm^{-1} vw.

2c. Cp_2WH_2 Reactions with 4-Methylbenzenediazonium Ion.

$[Cp_2WH(NNHC_6H_4\text{-}4\text{-}CH_3)]PF_6$, 14d, was synthesized from 4-methylbenzenediazonium hexafluorophosphate (111 mg, 0.42 mmole) and Cp_2WH_2 (133 mg, 0.42 mmole) in the manner of 14e; 71% yield. IR: 3265 w, 3133 wm, 2923 vw, 2874 vw, 1632 sh, 1601 wm, 1510 m, 1433 m, 1388 m, 1361 m, 1222 wm, 1171 vw, 1113 w, 1076 w, 1020 w, 849 sh, 832 vs, 757 w, 739, 729 wm, 633 w, 558 s, 503 cm^{-1} wm.

$[Cp_2WH(^{15}NNC_6H_4\text{-}4\text{-}CH_3)]BF_4$, 14c-$^{15}N(1)$, was synthesized from ^{15}N-4-methylbenzenediazonium tetrafluoroborate (58 mg, 0.28 mmole) and Cp_2WH_2 (89 mg, 0.28 mmole) in the manner of 14e but because a solid did not form during evacuation, the isolate collected was simply the involatile residue. IR: 3388 vw (trace 15c), 3237 wm, 3123 m, 3060 sh, 2924 w, 2870 sh, 1610 wm, 1406 s, 1431 wm, 1475 m, 1332 m, 1286 wm, 1220 wm, 1170 wm, 1085 s, 1055 s, 1012 s, 847 m, 829 m, 814 m, 758 w, 738 wm, 634 vw, 522 w, 506 cm^{-1} wm.

A similar reaction in an ice bath produced no yellow solid from $4\text{-}CH_3C_6H_4N_2BF_4$ (115 mg, 0.56 mmole) and Cp_2WH_2 (177 mg, 0.56 mmole), but after evaporation under vacuum for 1.0 h a brown oil was apparent. With continued stirring and evaporation this solidified, at which point the remaining solution was filtered off and further evacuated to dryness, leaving a trace of red oil. The brown solid 15c was recrystallized from propanone/toluene. Decomposed without melting above 333 K in air. IR: 3298 s, 3235 m, 3158 sh, 3116 m, 3018 wm, 2923 wm, 2863 w, 1607 s, 1571 wm, 1504 vs, 1436, 1422 m, 1322 vs, 1305 s, 1287 s, 1183 wm, 1085-1045-1020-1000 br vs, 930 m, 890 wm, 842 m, 810 s, 776 m, 690 w, 524 m, 370 cm^{-1} wm.

When stirred in degassed methanol in light at room temperature for 0.3 h no decomposition was detected, but over longer periods a slow decompostion to a black insoluble solid occurred. Like 17a the solid had no obvious infrared νNH but was not further characterized. When a sample of recrystallized material was treated with degassed methanolic HBF_4 (1 ml) no color change was apparent and no solid formed. In an earlier attempt nothing was precipitated by addition of ether so the methanol was removed under vacuum. This left a purple oil, 18, which was well evacuated, triturated with hexane and then ether with no effect and finally crystallized from propanone/ether as a deep purple solid. Anal. Found: C, 27.3; H, 3.14; N, 3.58. Calcd. for $[Cp_2W(NH_2NHC_6H_4Me)][O(HBF_4)_3]$: C, 28.5; H, 3.24; N, 3.91. IR: very broad background 3650-2500 with maximum possibly near 3200; 3340 m, 3220 m, 3130 s, 1633 br wm (νNH_2), 1587 wm, 1532 wm, 1515 s, 1433 s, 1364 m, 1364 m, 1296 wm, ca. 1075 vvs (νBF_4), 865 s, 838 sh, 807 m, 765 m, 579 w, 531, 523 wm, 486 cm^{-1} wm. Addition of a few drops methanol to a propanone solution of 18 caused rapid change to brown. The reaction could not be successfully repeated by ~~adding~~ 1 d 48% HBF_4. Though the purple oil formed with low quantity of hydroxylic solvent, reaction continued under evacuation or in air to give an amorphous brown solid mixture, part of which was extremely soluble in polar organic solvents.

2d. Cp_2WH_2 Reactions with 4-Methoxybenzenediazonium Ion.

When solid $4\text{-}CH_3OC_6H_4N_2BF_4$ (98 mg, 0.44 mmole) was added slowly over 1.0 h at 200 K to a solution/suspension of Cp_2WH_2 (140 mg, 0.44 mmole) in methanol (15 ml) the solution became orange very slowly, then 0.4 h after the last addition became yellow again, with yellow solid present throughout. Some of this was collected by tipping the reaction flask, letting solid settle in one neck and then decanting solution away, all at 200 K. This was later collected and shown by infrared to be a mixture of largely uncombined reactants. The solution and the rest of the suspended solid was allowed to warm. Near 273 K the solution turned orange-brown and an off-yellow solid formed. The solvent was removed with stirring, keeping the reaction flask below 273 K until all solvent had been lost. The yellow solid 14b was characterized without recrystallization. IR: 3236 m, 3120 m, 2833 w, 1611 vw, 1602 w, 1504 vs, 1463 m, 1436 s, 1395 s, 1361 s, 1300 m, 1245 vs, 1180 m, 1100-1010 vs, 847 s, 830 vs, 766 w, 728 m, 629 wm, 535 wm, 521 m, 447 wm, 374 w, 366 cm^{-1} vw.

When yellow 14b was dissolved in methanol, ethanenitrile, or propanone at room temperature, it readily converted to brown 15b, and also deposited dark insoluble solid, presumably 16 and/or 17. Solid 15b was collected by evacuating the filtrate to dryness. It was recrystallized from propanone/toluene. IR: 3303 m, 3237 m, 3100 m, 2950 sh, 2836 w, 1608 m, 1577 sh, 1503 vs, 1464 m, 1440 s, 1421 sh, 1316 m, 1278 s, 1241 vs, 1183 m, 1084-1032 vs, 930 sh, 890 sh, 824 s, 774 s, 600 w, 524 m, 375 cm^{-1} w.

3. Cp_2MoH_2 Reactions

Freshly distilled 2-propanol (25 ml) was transferred under vacuum to Cp_2MoH_2 (56 mg, 0.25 mmole) and stirred in an ice-salt bath as solid $4\text{-}FC_6H_4N_2BF_4$ (51 mg, 0.24 mmole) was added. The solution color during reaction appeared reddish, but was brown after 0.5 h. A solid filtered from solution under nitrogen had an infrared spectrum close to that of the reactant diazonium salt, e.g. ν NN 2285 and aryl-F 1230 cm^{-1}. The residue after removing all volatiles under vacuum at ambient temperature had a considerable amount of material whose infrared spectrum mimics 15: 3300 m, 3240 m (νNH_2); 3110 s (νCH); 1600 m (δNH_2 and νC=C aryl); 1495 vs, 1440 m, 1425 m (νC=C aryl and Cp); 1365 wm, 1315 m, 1270 m; 1214 s (νaryl-F); ca. 1050 vvs, v br (νBF_4); 823 vs (δ 1,4-aryl); 778 s; 518 m (νBF_4); 468 wm; 390 wm; 327 cm^{-1} wm. Anal. Found: C, 42.3; H, 3.97; N, 4.43. Calcd. for $[Cp_2MoNH_2NC_6H_4F)]BF_4$: C, 43.9; N, 3.68; N, 6.39. PMR ($(CD_3)_2CO$) of a similar sample prepared in methanol (Anal, Found: C, 41.6; H, 3.57; N, 6.57): 7.67-5.90 m aryl and impurities; 5.63 s Cp; 3.32 and 3.18 MeOH; with expected NH_2 lost in noise.

During slow addition of $4\text{-}FC_6H_4N_2PF_6$ (130 mg, 0.48 mmole) to Cp_2MoH_2 (132 mg, 0.58 mmole) in methanol stirred at 200 K the solution developed a moderately intense rust color. After 4 h stirring some of the unreacted Cp_2MoH_2 was removed by decanting and the solvent removed overnight as the bath slowly warmed to room temperature. The brown residue was washed with benzene to remove remaining Cp_2MoH_2. Anal. Found: C, 37.0; H, 3,23; N, 4.24. Calcd. for $[Cp_2MoNH_2NC_6H_4F)]PF_6$ C, 38.7; H, 3.25; N, 5.65. The infrared spectrum of the residue agrees with that of the material above except for a shift in νNH and replacing νBF_4 with νPF_6, which allows observation of any absorption near 1050 cm^{-1}: 3330, 3250 m (ν NH); 1160 wm, 1100 wm, 1065 wwm, 1020 m, 1006 m; ca. 840 vvs, 740 s, 555 cm^{-1} vs (νPF_6). PMR (CD_3CN) had two strong singlets at 7.33

(benzene) and 5.64 (Cp). The region between 7.30 and 5.16 contained a forest of peaks and accounted for 60% of the integrated intensity of the complex. This was taken to be the spectrum of a significantly decomposed material in which decomposition has involved the cyclopentadiene ligands.

The 1:1 addition of 4-fluorobenzenediazonium tetrafluoroborate or hexafluorophosphate to Cp_2MoH_2 was done five times. By far the most successful, at least as indicated by infrared spectra of the unrecrystallized products, were those just described. In no case was the crude product successfully reprecipitated. In methanol or propanone solution the product mixtures decomposed to a material with medium to strong intensity absorption at 3330 cm^{-1}, and brown solid $\underset{\sim}{20}$ was occasionally collected. One such sample was precipitated from methanol/benzene. Anal. Found: C, 29.7, H, 3.21; N, 4.55. Calcd. for "$C_{16}H_{16}N_2FMo(BF_4)_{3.4}$", C, 29.7, H, 2.5; N, 4.3. IR: ca. 3400 sh (ν OH); 3335 m (ν NH); 3110 m (ν CH); ca. 1610 (δ OH_2); 1500, 1485 sh, 1425 m, 1080 s (ν BF_4); 834 (δ 1,4-aryl); 560 br wm; 528,518 cm^{-1} (ν BF_4). Other decomposition/oxidation products formed, but were never characterized.

When addition of solid 4-methoxybenzenediazonium tetrafluoroborate (152 mg, 0.68 mmole) to a methanol (30 ml) solution/suspension of Cp_2MoH_2 (157 mg, 0.69 mmole) was done at 200 K during only 0.25 h, the solution turned very intensely red. The yellow solid Cp_2MoH_2

took 1.5 h to disappear, and at that time the presence of a considerable amount of dark solid was first noted. Purple solid **21b**, $[Cp_2MoH_2 \cdot 2\ NNC_6H_4OMe](BF_4)_2$, was filtered out after 2 h, washed once with methanol (giving a deep red washing), and dried under vacuum. The volatiles were stripped from the filtrate, and the crude isolate purified by trituration with toluene and then THF. An infrared of this material indicated the presence of **19b**, $[Cp_2Mo(NH_2NHC_6H_4OMe)]BF_4$: νNH_2 3300, 3240 m; 1600 cm^{-1} wm. Another spectrum taken after the sample had remained in the dry box over three years indicated complete decomposition to **20**. The only obvious differences in the infrared spectra of these samples of **19** and **20** are the presence of νNH at 3340 cm^{-1} in **20** in place of the two lower frequency bands in **19** and a shift in the $\nu C{=}C$ aryl mode from 1490 in **19** to 1510 cm^{-1} in **20**.

Solid **21b** was found to decompose above about 398 K and to be insoluble in benzene, carbon tetrachloride, and water; very slightly soluble in ether and glacial acetic acid; slightly soluble in chloroform and dichloromethane and very soluble in propanone and acetonitrile. Λ_M (CH_3CN, 298. K) 243 $ohm^{-1}cm^2mole^{-1}$. In this solvent conductivities of 1:1 electrolyte complexes range between 120 - 160 $ohm^{-1}cm^2mole^{-1}$; 2:1 electrolytes range roughly between 220 - 300 $ohm^{-1}cm^2mole^{-1}$. IR: 3124 m (νCH); 2940 sh, 2840 w (νCH_3); 1598 vs, 1575 m, 1535 wm, 1504 s, 1487 m, 1468 m, 1444 m, 1420 m, 1310 m, 1265 vs, 1165 vs, 1080-1050 vs, 834 s, 765 wm, 520 cm^{-1} m. The intensity of the peak near 1600 cm^{-1} easily distinguishes this from the material of the filtrate.

Synthesis of 21b was repeated using 65 mg (0.3 mmole) Cp_2MoH_2 and 121 mg (0.545 mmole) diazonium salt, which gave 70 mg methanol-insoluble product. Anal. Found: C, 43.3; H, 3.82; N, 8.57. Calcd. for $[Cp_2MoH_2 \cdot 2\ NNC_6H_4Me](BF_4)_2$: C, 42.9; H, 3.90; N, 8.37. Infrared does not agree entirely with that just above: 1535 s, 1504 absent, 1487 vs, 1310 shifted to 1298, 1265 shifted to 1250, new peak at 1180 m, 765 absent, new 735 wm, new 662 wm, new 530 m. Differences are probably due to the presence of 19b in the product obtained from the reaction above, in which only one mole diazonium salt was used per mole Cp_2MoH_2.

4. Cp_2ReH Reactions

$[Cp_2Re(NHNC_6H_4\text{-}4\text{-}F)]PF_6$, 22e. Solid 4-fluorobenzenediazonium hexafluorophosphate (62 mg, 0.23 mmole) was added in portions to a solution/suspension of biscyclopentadienylrhenium hydride (77 mg, 0.24 mmole) in 20 ml of cold (T < 273 K) methanol under vacuum. The solution became red and then brown. Following addition over 0.4 h and further stirring over 0.1 h, the solution was cooled with liquid nitrogen until frozen. No loss of vacuum was detected. The solvent was evaporated under vacuum leaving a brown, amorphous solid. The solid was recrystallized below 273 K with ethanenitrile (1 ml)/ether(15 ml). Anal. Found: C, 32.9; H, 2.74; N, 4.64. Calcd.

for $C_{16}H_{15}N_2F_7PRe$: C, 32.8; H, 2.58; N, 4.78. IR: 3223 vw (νNH), 3135 m (νCH), 1499 vs (νCC Cp and aryl); 1230 s (νaryl-F), ca. 835 vvs (ν PF_6 and δ 1,4-aryl). PMR (CD_3CN): 7.16, 7.06 pseudo d [4 H], aryl; 5.79 s [10 H], Cp; 5.62 s [3-4 H], ?; 4.84 s [2-3 H], impurity. Decomposition of the cold solution occurred over eight days with decreasing relative intensity of all peaks except that at δ 4.84. At six days new peaks had appeared at δ 7.48 and 7.36 but then these also became lost in noise. An infrared of material present in the filtrate left from recrystallization had a strong peak ca. 1660 cm^{-1}. This is assigned as due to a product with two moles of diazonium salt. (See below.)

$[Cp_2Re(NHNC_6H_4\text{-}4\text{-}OCH_3]BF_4$, 22b, was synthesized similarly except that the solution was held at 273 K during addition and became intensely brown immediately. The solid was triturated with hexane, but not recrystallized before analysis. It was soluble in ethanenitrile, propanone, methanol; moderately soluble in cyclohexanone, dichloromethane, chloroform, 1-propanol; insoluble in toluene, ether, hexane. The solid was difficult to recrystallize for concentrated solutions were so intensely colored as to be opaque and more dilute solutions were incompletely precipitated by addition of a poor solvent. The isolate which was purest was obtained as the least or slowest-soluble material from propanone, though this was obviously not efficient. IR: 3195 wm (νNH); 3120 m (νarylH); 2925, 2835 wm (ν alkylH); 1600 wm, 1500 s (νC=C aryl and Cp); 1250 vs (νC-O-Me); ca.

1050 vvs br (νBF_4); 830 s (δ 1,4-aryl). PMR (CD_3CN): 11.5 v br, NH; 7.0 m at 60 MHz or pseudo q with J= 9 Hz at 100 MHz [4 H] aryl; 5.77 s [10 H] Cp; 4.85 s [1 H] impurity; 3.78 s [3-4 H] OCH_3. PMR ($(CD_3)_2CO$): δ 12.1 v br NH; 6.92 m aryl; 5.96 s Cp; 5.58 and 3.90 impurity; 3.77 s OCH_3.

$[Cp_2Re(NHNC_6H_4\text{-}4\text{-}CF_3)]BF_4$ was synthesized similarly except that the reaction was done with 10 ml methanol at room temperature. IR of toluene triturated crude material: 3210 w br (νNH); 3135 m (νarylH); 1660 wm sh impurity; 1612 s, ca. 1590 sh, 1500 m (νC=C aryl and Cp); 1410 s (νC-C aryl and Cp); ca. 1315 vs (νCF_3); ca. 1050 vvs br (νBF_4); 840, 815 s (δ 1,4-aryl). The product was lost when recrystallization was interrupted by a lengthy power failure but the low intensity of the band at 1500 cm^{-1} implied that this synthesis might not have been as successful.

1:2 Reaction. One attempt was made by Dr. Alan Gilchrist to synthesize a 1:2 product by simply adding a second mole of 4-methoxybenzenediazonium tetrafluoroborate after the first had been added and given 0.1 h to react. The isolate obtained by stripping off all solvent and triturating with ether was brown-black. A sample was recrystallized from 5 ml propanone/1 d 48% aq. HBF_4/2 ml CH_2Cl_2/ether added slowly until solidification. The solid was washed with ether and vacuum dried. Anal. Found: C, 40.4; H, 3.54; N, 6.64. Calcd. for $[C_{24}H_{25}N_4B_2F_8O_2Re]$: C, ~~37.9~~; H, 3.31; N, 7.36. The infrared spectrum has a strong band at 1660 cm^{-1} and other absorption at 1580 m, 1498 vs (ν C=C); 1258 (ν C-O-Me); but only medium intensity at 1050 where νBF_4 is expected to absorb strongly. The analytical formulation as a 1:2 adduct must be treated as merely suggestive.

$[Cp_2Re(NNC_6H_4\text{-}4\text{-}OMe)]$, 23. A degassed solution of 0.05 M potassium carbonate in methanol/water was added to solid $[Cp_2Re(NHNC_6H_4\text{-}4\text{-}OMe)]BF_4$ under nitrogen. The mixture was stirred vigorously 10 min and 1 ml H_2O added to precipitate the brown product, which was washed with water and vacuum dried. IR: ca. 3070 w (ν aryl-H); ca. 2920 w, 2830 w (ν alkyl-H); 1610 s (ν NN); 1580 m, 1492 vs (ν C=C); 1245 (ν C-O-Me); 1180 m, 1025 m, 905 m; 828 (δ 1,4-aryl). The solid 22b did not react as an ether suspension with triethylamine, but in solution did so, producing 23 and Et_3NHBF_4, identified by comparison of its infrared spectrum with an authentic sample.

Chapter V.

Ligand Abstraction in the Reactions of Diazonium Ions with Iron Complexes of 2,3-Dimercapto-2-butenedinitrilate(2-).

A. Introduction

Considerable study since 1957 within the field of inorganic chemistry has been done on metal thiolate complexes.[217] Currently, the most noteworthy results concern monomeric, dimeric and tetrameric iron complexes which model[218] and include the electron transfer sites of the so-called non-heme iron proteins.[219] A direct antecedent to these is the study of the oxidation-reduction reactions possible with metals complexed by 1,2-ethenedithiolate-type ligands. Complexes of the general forms $\{M(S_2C_2R_2)_2\}^{n-}$ and $\{M(S_2C_2R_2)_3\}^{n-}$ were intriguing because, among other things, they can be oxidized/reduced through as many as three different stable oxidation states, with polarographic evidence for the existence of more.[220]

Compounds of $[M(NO)(S_2C_2R_2)_2]^{n-}$ are also found to be readily oxidized and reduced.[221] Study of the moderately stable complexes in different oxidation states gives a sizable variety and quantity of data (electrode potentials, magnetics, UV, ir) with which one can determine their electronic structures. Thus, this sort of complex appeared to be an unusually attractive candidate for comparing the bonding and electronic structure of M-NO with M-NNAr.

The obvious problem was synthesis of $[Fe(NNAr)(S_2C_2R_2)_2]^{n-}$. The nitrosyl analogues had been synthesized from NO gas. As noted in Chapter I, there is no comparable route for diazo complexes. The reaction of anionic $[\{Fe(S_2C_2(CN)_2)_2\}_2]^{2-}$,[220] which will be abbreviated as simply $\{Fe(mnt)_2\}^-$, with a cationic diazonium salt was found to lead to ligand abstraction. Preliminary attempts at other synthetic routes (reaction of diazonium with the nitrosyl complex $[Fe(NO)(mnt)_2]^-$; replacement of phosphines and carbonyls from $[Fe(CO)_2(NNAr)(PPh_3)_2]^+$ with oxidation; complexation of phenylhydrazine to be followed by oxidation; reaction of aniline with $[Fe(NO)(mnt)_2]^-$) showed no promise. The original aim of this study being entirely thwarted by an inability to synthesize the required aryldiazenido complexes, we report[93] only the synthesis of new thioethers derived from cis-2,3-dimercapto-2-butenedinitrilate(2-), known also as maleonitriledithiolate or cis-1,2-dicyanoethylene-1,2-dithiolate.

B. Results and Discussion

When combined in methanol, the two soluble salts $Na\{Fe(mnt)_2\}$ and $[4\text{-}Et_2NC_6H_4NN]BF_4$ undergo metathesis and a compound of empirical formula $[4\text{-}Et_2NC_6H_4NN][Fe(mnt)_2]$ precipitates. The solid state infrared spectrum has no absorption between 2100 and 1600 cm^{-1}, the region in which $\nu(N{=}N)$ of a bound aryldiazenide might appear, and we assign a peak at 2140 cm^{-1} to $\nu(N{\equiv}N)$ by comparison with the diazonium tetrafluoroborate. This solid is stable at room temperature. It is an example of an unusual, large counterion stabilizing the diazonium cation. It would not be especially noteworthy except that its formation contrasts with the reaction of diazonium cations having less π-donating para substituents.

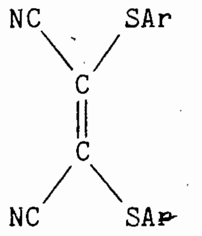
When a similar combination of $NaFe(mnt)_2$ and 4-F- or $4\text{-}MeO\text{-}C_6H_4NNBF_4$ is attempted, a smooth bubbling is seen and with excess diazonium salt the intense color of the solution, characteristic of transition metal complexes of the ligands $S_2C_2R_2^{2-}$,[222] is sharply reduced. The insoluble residue left after solvent evaporation yielded a yellow benzene or toluene extract. Repeated crystallizations from small volumes of solvent allowed separation of $4\text{-}RC_6H_4SC(CN){=}C(CN)SC_6H_4\text{-}4\text{-}R$, 24. (See listing, Table V-1.) Since infrared spectra of the crude extract and the crystals matched well, it appears that the crude extract is substantially 24 and that 24 is a major product of the reactions, though only small quantities of crystalline material were ever recovered.

Table V-1. Analytical Data for 24, $(4\text{-}RC_6H_4S)_2C_2(CN)_2$.

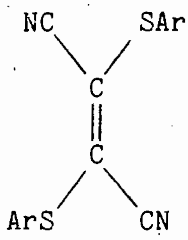
Compound	Analytical Data						M.P.	Parent
	Found			Calculated			(°C)	m/e
	C	H	N	C	H	N		
24a R=F	56.90	2.33	8.47	58.17	2.44	8.48	145	330
24b R=OMe	24.04	4.00	8.01	24.19	3.97	7.86	156	354
24c R=Et_2N	64.78	6.36	12.44	66.01	6.46	12.83	137	436

When the aforementioned $[4\text{-}Et_2NC_6H_4NN]\{Fe(mnt)_2\}$ is heated in methanol with three moles of diazonium salt, the analogous product is isolated by the same work-up. A slow reaction of two moles $4\text{-}Et_2NC_6H_4NNBF_4$ per mole $Na\{Fe(mnt)_2\}$ at room temperature produces a similar material, but analyses (C, 52.16; H, 4.38; N, 15.96%) suggest considerable contamination with a material of empirical formula HSC(CN). No evidence for novel products, particularly aryldiazenido complexes, was noted with this stoichiometry and mild reaction conditions.

Infrared spectra (Figure V-1) of the compounds 24 are quite similar, allowing for the change in ring substituent. The strong absorption near 1500 cm^{-1} is assigned to νC=C of the butenedinitrile, though some aryl intensity can not be excluded. The assignment requires that the similar groups lie at cis sites,



cis-24



trans-24

since the trans form is centrosymmetric and would not have an infrared active νC=C. The long wavelength ultraviolet absorptions of 24a and b (Figure V-2) match closely the absorption of cis-MeSC(CN)=C(CN)SMe and are at higher energy than trans-MeSC(CN)=C(CN)SMe.[223] This is further evidence for cis stereochemistry in 24.

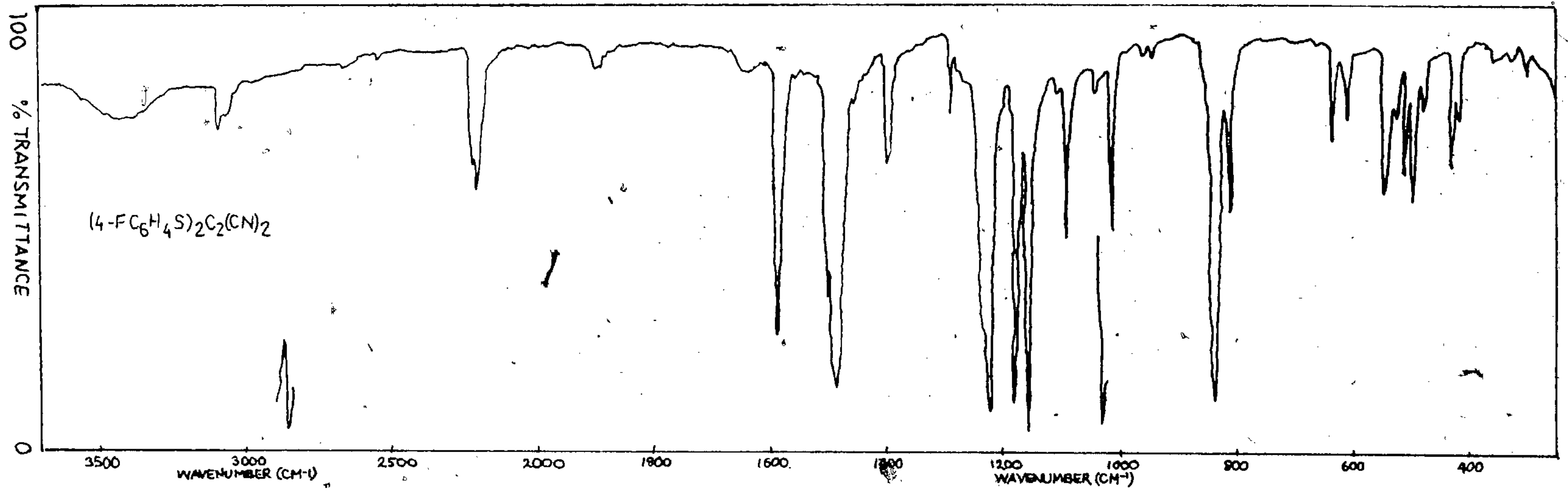


Figure V-1. Infrared Spectrum of $(4\text{-}FC_6H_4S)_2C_2(CN)_2$.

Though 2,3-di(alkylthio)butene derivatives had been known, including RSC(CN)=C(CN)SR,[224] the aryl derivatives were not previously reported.

The compound $Et_4N[Fe(NO)(mnt)_2]$ was made to see if the coordination of NO would alter the site of attack of diazonium from sulfur to iron. Only one mole of 4-fluorobenzenediazonium salt was used. Infrared of the crude solid obtained by removing all volatiles had little NO intensity of the initial nitrosyl complex, and an absorption at 1830-1800 cm^{-1}. Since extraction of the solid with benzene separated 24a, showing that the diazonium ion attacked at the sulfur rather than iron, the new infrared absorption is likely to be a nitrosyl stretch. No iron complex was isolated, and the reaction seems not to be productive. (See also the Appendix for reaction of $[Fe(NO)(mnt)_2]^-$ with aniline.)

The reaction of $[Fe(mnt)_2]^-$ or $[Fe(NO)(mnt)_2]^-$ could be either an electron transfer to the diazonium cation, nucleophilic attack, or more likely, both.[225-7] Electron transfer would produce an aryldiazenyl radical, which would rapidly lose dinitrogen. Attachment of the aryl radical to a sulfur would lead to 24. Since little fluorobenzene was produced, either the scavenging by sulfur must be efficient, or the proportion of ArN_2^+ reacting by electron transfer must be low. The outline of a nucleophilic mechanism is: attack of electron density located at a sulfur on the terminal aryldiazonium nitrogen and, in either order, decomplexation of sulfur and extrusion of dinitrogen, leaving 24.

Compounds 24 can also be synthesized directly from $Na_2S_2C_2(CN)_2$. This salt reacts easily at room temperature with $4\text{-}FC_6H_4NNBF_4$. The reaction appears to be less clean than that of the iron complex. Again, small amounts of pure 24a were isolated by repeated slow crystallization. There is a large amount of deep red tar also produced. Electron transfer may be more important in reaction of the uncomplexed thiolate since $Na_2S_2C_2(CN)_2$ is a reasonably good reducing agent.[223] In one trial twice as much mass was lost (measured as the difference between the sum of the reactant masses and the mass of the vacuum-dried product) as expected simply from the complete loss of dinitrogen. We suppose the difference is the mass of fluorobenzene produced by a radical process.

A recent communication suggests that diazonium salts are reduced to arylhydrazines by selenols.[227] In only one instance did we detect evidence of a hydrazine product. In a preliminary reaction using unmeasured quantities and adding solid diazonium salt to a methanolic solution of $Na\{Fe(mnt)_2\}$ until the solution color was yellow, the dry residue left after precipitating excess diazonium salt and removing other tetrafluoroborate salts by water extraction had medium intense absorptions at 3340, 1620, and 1515 cm^{-1}.

In Chapter VI are reported the reactions of $\{Fe(CO)_3SMe\}_2$ with diazonium salts. These complexes are not attacked at room temperature. Thus ligating sulfur atoms are not necessarily sufficiently nucleophilic to attack diazonium cations. Obviously the nucleophilicity in the maleonitriledithiolate complexes is greater and is centered at the sulfur rather than the iron. Molecular orbital calculations have suggested that the highest filled levels of $[Ni(mnt)_2]^{n-}$ complexes have a high degree of ligand character.[220] Our results give chemical support to this and suggest that the statement is still applicable with change of metal at least as far as iron. Thus we did not even try initially envisioned extension to cobalt complexes. And similarly we did not feel that the iron of $[Fe(mnt)_2]^{2-}$ would be sufficiently nucleophilic to compete productively with the ligating sulfur.

Another method of synthesis of $[ArNNFe(mnt)_2]^{n-}$ which was attempted was displacement of CO and PPh_3 from $[Fe(CO)_2(NNAr)(PPh_3)_2]BF_4$ by $Na_2S_2C_2(CN)_2$. The two salts did not appear to react at room temperature. With heating CO was evolved (νCO was not seen in the crude product) but no pure substance was separated in our attempts. Other routes to $[Fe(NNAr)(S_2C_2R_2)_2]^{n-}$, such as oxidation of the (unknown) compound $[Fe(NH_2NHAr)(S_2C_2R_2)_2]^{n-}$ do not seem any more promising.

Our results can not reliably be applied to evaluation of the role of sulfur in possible mechanisms of nitrogenase function. There are four different types of iron sites in reduced nitrogenase. Most, if not all, the iron is sulfur-bound.[228] But beyond this very little is known with any certainty about the iron coordination, and nothing is known about the possible state of a dinitrogen intermediate that could react with sulfur-bound iron.

C. Experimental

1. General

Instrumentation and general procedures were the same as reported in Chapter III. Tetraethylammonium chloride and nitrogen monoxide were commercial samples used without further purification. Diazonium salts were prepared as described above. $Na_2S_2C_2(CN)_2$,[222] $(Et_4N)_2[FeNO(mnt)_2]$,[221] and $Et_4N[Co(mnt)_2]$ [222] were prepared by literature methods with no significant variation.

$Na_2[\{Fe(S_2C_2(CN)_2\}_2]$ was prepared by addition of $Na_2S_2C_2(CN)_2$ (4.03 g) to iron(III) chloride (1.73 g), each in 50 ml water. The solution of ligand salt was protected from light before addition. A black precipitate of the product formed steadily. This was filtered, washed well with water and dried to a constant weight over P_2O_5. Yield 2.26g.

$Et_4N[FeNO(mnt)_2]$ was prepared by the method of McCleverty[221] from $Na\{Fe(mnt)_2\}$ (1.02 g) in 55 ml propanone by reaction with NO gas mixed with N_2 over 2.5 hr. After N_2-purge, Et_4NCl (0.53 g) was added, the liquid volume reduced to less than half on a rotary evaporator, and the solution cooled to ca. 263 K. The black precipitate was filtered and washed three times each with cold methanol and ether. Yield 0.668 g. Anal. Found: C, 39.09; H, 4.18; N, 16.81. Calcd. for $(C_2H_5)_4N[FeNO(S_4C_4(CN)_4]$: C, 38.71; H, 4.06; N, 16.95. Electronic and infrared spectral data agree with those tabulated in reference 221 except that no peak at 1716 cm^{-1}, probably from retained propanone, was detected in our spectra.

2. Reactions of Na{Fe(mnt)$_2$}

Solid $4\text{-}FC_6H_4NNBF_4$ was added in small portions to a stirred solution of $Na\{Fe(S_2C_2(CN)_2)_2\}$ (382 mg, 1.06 mmole) in 15 ml methanol. During addition of the first 4 mmole of diazonium salt, obvious bubbling occurred as the salt dissolved, and solution color changed from deep red to orange. After this point added diazonium salt was slow to dissolve and did not seem to react. After two days all volatiles were removed through a liquid N_2 trap. A UV spectrum of this trapped material showed only 0.5 mmole C_6H_5F, calculated from literature values[229] of extinction coefficients (λ_{max}= 278(sh), 265.5, 260, 254, 248.5, 243(sh) nm). Evaporation of the toluene extract of the involatile residue left 24a as a waxy yellow material. Solid 24a was obtained from concentrating a CH_2Cl_2 solution by bubbling argon through it then cooling to ca 263 K. The solid was washed with CCl_4. Infrared spectrum (4000-400 cm^{-1}): 3100, 3080 vw (νCH); 2230, 2220 wm (νCN); 1590 m, 1400 wm (νCC arom.); 1490 s (νC=C butenedinitrile); 1295 w; 1225 s (νCF); 1180 s, 1160 s, 1095 m, 1015 m; 840 s, 815 m sh

(δ CH of 1,4-disubst. arom.); 635 wm, 610 w (CS); 545 wm; 515 wm, 500 wm (δ CCN); 430 wm, 420 cm^{-1} w. Electronic spectrum (in CH_3OH; λ_{max} in nm ($\log_{10} \epsilon$)): 334 (4.18), 248 (3.94), ca. 221 (4.28).

After toluene extraction of the involatile material, it was extracted with propanone, leaving a mixture of brown and white salts. The white was water soluble $NaBF_4$. After oven drying, the brown was characterized by a positive qualitative acidic-thiocyanate test for Fe(III), and by infrared (KBr): the only absorptions are 3300 wm vbr (νOH···O); 1610 w br (δ. OH_2); 1080 wm br ($\nu FeOH_2$); and 515 cm^{-1} m br (νFeO). The propanone-soluble material contained two more fractions: (a) An unidentified material not precipitated from cold propanone/ether. Infrared spectrum (KBr): 3210 m br; 2220 wm (νCN nitrile); ca. 1725-1620 w sh, 1585 m, 1490 m; ca. 1450, 1400, 1350 w sh; 1295 wm; 1230 m, 1090 vs; 1060 vs (νBF); 1040 vs, 835 m; 535, 525 m (νBF); 290 cm^{-1} wm. (b) An iron-free material which crystallized from propanone/ether or methanol/ether when cooled and which coupled with beta-naphthol to make an orange solid exactly like a $4\text{-}FC_6H_4NNBF_4$ standard, but which had somewhat different infrared and UV spectra from and lower decomposition/melting point (139°C) than the authentic material (164°C). Spectral properties were unchanged by treatment of a propanone solution with charcoal. Anal. Found: C, 36.44; H, 2.71; N, 13.09. Calcd. for $C_6H_4N_2BF_5$: C, 34.33; H, 1.92; N, 13.35. Infrared spectrum: 3150 w, 2260 m, 1585 wm, 1440 w, 1340 w, 1285 m, 1255 m, 1100 s, 1080 s, 1060 s, 1010 m, 845 wm, 525 cm^{-1} wm.

Electronic spectra: in CH_3CN 311.5 (4.1), 268 (3.5), 231 nm (3.6); same position and relative intensities in CH_3OH. The electronic spectra of $4\text{-}FC_6H_4NNBF_4$ for comparison: in CH_3CN 265 (4.1); in CH_3OH ca. 305 (3.2), 266 nm (3.5).

$(4\text{-}CH_3OC_6H_4S)_2C_2(CN)_2$ was prepared at room temperature by adding dropwise to a solution of 76 mg Na{Fe(mnt)$_2$} in 3 ml dimethylsulfoxide a solution of a large excess of $4\text{-}CH_3OC_6H_4NNBF_4$ in 1 ml dmso until no bubbling or color change was noted with an addition. Solvent was removed on the vacuum line. The residue was extracted with toluene. Cooling the filtrate of a solution in a minimum volume (2-3 ml) of hot (333 K) toluene and passing argon over the surface gave lightly colored crystals. Hexane was added to increase the quantity of solid, which was then filtered and washed with hexane. Electronic spectrum in CH_3OH: 339 (4.4), 288 (4.2), 241 nm (4.6). Infrared spectral features: 2960, 2840 w (νCH alkyl); 1495 s (νC=C butenedinitrile); 1254, 1245 s (νCOMe); 1170 vs; 835 s, 815 wm (δ CH of 1,4-disubst. arom.).

Stirring a mixture of Na{Fe(mnt)$_2$} (163 g, 0.458 mmole) and $4\text{-}Et_2NC_6H_4NNBF_4$ (484 g, 1.84 mmole) in 10 ml methanol at room temperature for 2 h produced a yellow solution and a black insoluble solid which was removed by filtration. Anal. Found: C, 41.65; H, 2.61; N, 18.56. Calcd. for $[Et_2NC_6H_4NN][FeS_4C_4(CN)_4]$: C, 42.19; H, 2.75; N, 19.13. Infrared spectrum (KBr): 3105 w, 3075 w (νCH arom.); 2975, 2920, 2850 wm (νCH ethyl); 2240 wm, 2140 vvs (νNN), 2205 s (νCN nitrile); 1585 vvs, 1533 m (νCC arom.); 1487 s (νCC butene); no appreciable νBF_4 ca. 1050; 813 s (δ 1,4-disubst. arom.); 375 cm^{-1} m (νFeS).

24c was produced by heating $4\text{-}Et_2C_6H_4N_2]\{Fe(mnt)_2\}$ with three moles 4-diethylaminobenzenediazonium tetrafluoroborate in methanol (323-338 K) for two days, removing methanol under vacuum, extracting the involatile residue with benzene, crystallizing from evaporating CCl_4, filtering, and washing with methanol. Electronic spectrum in CH_3CN: 402 (3.9), 325-300 nm (broad plateau of unresolved peaks, $\log_{10}\epsilon$ 4.5 at 315 nm). Infrared spectral features: 2970 m, 2930, 2900 wm, 2870 w (CH alkyl); 1510 s (νC=C butenedinitrile); 810 m (δ CH of 1,4-disubst. arom.).

3. Reaction of $Et_4N[FeNO(mnt)_2]$

An equimolar amount of solid $4\text{-}FC_6H_4NNBF_4$ was added in small portions to $Et_4N[Fe(NO)(mnt)_2]$ (1.00 g) in 3 ml ethanenitrile. Bubbling was noted with each addition. The solution was allowed to stand 2 h before the solvent was removed under vacuum. An infrared spectrum of the crude material showed no νNN of residual diazonium and CF shifted down to 1230 cm^{-1}. The nitrosyl absorption of the reactant (1860 cm^{-1}) shifted to 1865(sh), 1830 and ca. 1800(sh). Extraction with benzene (4x1 ml) separated a material which was 24a by comparison of its color and infrared spectrum to those samples prepared from

Na{Fe(mnt)$_2$}. The black benzene-insoluble material was largely soluble in propanone, precipitating Et_4NBF_4 with addition of ether and cooling. The benzene and propanone insoluble light brown solid gave a positive acidic-thiocyanate test for Fe(III).

4. Reaction of $Na_2S_2C_2(CN)_2$

Dropwise addition of a yellow-green solution of $Na_2C_2S_2(CN)_2$ (0.091 g, 0.49 mmole) in 2 ml methanol to a solution of $[4\text{-}FC_6H_4NN]BF_4$ (0.203 g, 0.966 mmole) in 10 ml methanol produced a red solution with effervescence. After stirring 15 min the solvent was removed and the organic product separated from $NaBF_4$ as a benzene solution. Addition of cyclohexane to a concentrated benzene solution caused separation of a flaxen colored oil which has infrared bands at 2230 (νCN) and 1520 cm^{-1} (νC=C butenedinitrile) but no aromatic absorption. The benzene was stripped from the decantate and CCl_4 added, producing an uncharacterized dark red oil and a yellow solution. Crystals of 24a (MP 142°C) were obtained from the CCl_4-soluble fraction after evaporation, by recrystallization from methanol-water. Anal. Found: C, 57.84; H, 2.48; N, 8.59. Calcd. for $C_{16}H_8F_2N_2S_2$: C, 58.17; H, 2.44; N, 8.48. Infrared and electronic spectra identical to those of samples obtained from Na{Fe(mnt)$_2$}.

Chapter VII. Appendix

A. Reactions of Metal Nitrosyl Complexes toward Synthesis of Aryldiazenides.

1. $Na_2[Fe(CN)_5NO]\cdot H_2O$

a. Introduction

Probably the most-studied nitrosyl complex has been $[Fe(CN)_5NO]^{2-}$, the nitroprusside ion.[230] Since the nitrosyl group is the center of much of the chemistry and spectroscopy of this ion, the possibility of studying the aryldiazenido analogue was exceptionally inviting, especially at the time when this research was conceived to be a comparison between the two ligands.

The nitrosyl of nitroprusside is quite electrophilic. Its reaction with hydroxide is an example of this property.[230]

$$[(NC)_5FeNO]^{2-} + OH^- \rightleftarrows \{[(NC)_5FeN(O)OH]^{3-}\} \qquad (VI\text{-}1)$$

$$\{[(NC)_5FeN(O)OH]^{3-}\} + OH^- \rightleftarrows [(NC)_5FeNO_2]^{4-} + H_2O \qquad (VI\text{-}2)$$

With other bases electrophilic nitrosyl complexes have reacted in a variety of related ways.

$$Na_2[(NC)_5FeNO] + 2\ NaNHR \longrightarrow Na_4[(NC)_5FeN(O)NR] + NH_2R \qquad (VI\text{-}3)^{231}$$

$$[Ru(bipy)_2(NO)X]^{2+} + 2\ Me_2PhN \longrightarrow \qquad (VI\text{-}4)^{232}$$

$$[Ru(bipy)_2\{N(O)C_6H_4NMe_2\}X]^+ + Me_2PhNH^+$$

$$Na_2[(NC)_5FeNO] + NaSH + NaOH \longrightarrow Na_4[(NC)_5FeSNO] + H_2O \qquad (VI\text{-}5)^{230}$$

$$Na_2[(NC)_5FeNO] + 2\ NH_3 + NaOAc \longrightarrow \qquad (VI\text{-}6)^{233}$$

$$Na_3[(NC)_5FeNH_3] + N_2 + H_2O + HOAc$$

Reactions VI-3 and 4 are completely analogous to the hydroxide transformation of VI-1,2. Reaction VI-5 involves a rearrangement of the analogous product. Reaction VI-6 is qualitatively different from the others. It involves elimination of the nitrosyl oxygen as water, presumably via an intermediate with coordinated dinitrogen which is then substituted by ammonia. Kenney has also performed syntheses of primary alkylamine complexes of pentacyanoferrate(II) along this line.[233]

The diazenide $[RuCl(bipy)_2NNAr]^{2+}$ has been synthesized by the reaction:[234]

$$[RuCl(bipy)_2NO]^{2+} + ArNH_2 \rightarrow [RuCl(bipy)_2N_2Ar]^{2+} + H_2O \quad (VI-7)$$

So far this is the only metal nitrosyl which has been shown to react in this way. The synthesis parallels reaction VI-6 in that the nitrosyl is attacked by the amine, eliminating water. However the aryldiazenide is not lost in this case; substitution by aniline in the manner of Kenney's work does not occur.

We hoped to isolate an aryldiazenide complex from the reaction (Eq. VI-8) of nitroprusside with an aniline analogous to equation VI-7.

$$Na_2[(NC)_5FeNO] + NH_2R \rightarrow Na_2[(NC)_5FeNNR] + H_2O \quad (VI-8)$$

Though primary alkyl amines produced amine complexes,[233] the aryl ring may confer added stability to an aryldiazenide complex and allow its isolation before substitution by more aniline. Though $[(NC)_5FeNNR]^{2+}$ had not previously been identified, it must be realized that much of the related chemistry was either physically oriented or quite old. In the case of the former, there are examples of thorough kinetic studies of reactions from which actual products have not been identified;[235] and the earlier work, without the spectroscopic techniques available today, is not unlikely to include misidentified products. (See further section VI-A-1-c.)

As well as being an electrophile, nitroprusside can act as an oxidizing agent toward some potential nucleophiles.[230] The most recent electrochemical study,[236] combined with synthetic work,[237] makes a strong case for identification of a blue reduction product (λ_{max}= 606 nm, ν(NO)= 1755, ν(CN)= 2111, 2122(sh) cm^{-1}) as $[(NC)_4FeNO]^{2-}$. This had previously been most generally taken to be $[(NC)_5FeNOH]^{2-}$.[230] In more basic solutions a yellow-brown product is formed which is consistently supposed to be a salt of $[(NC)_5Fe(NO)]^{3-}$.[237]

Another potential source of experimental difficulty is that nitroprusside is sensitive to light. In spite of considerable past experience with the reactions, the substances produced in the photochemical reactions of $[(NC)_5FeL]^{n-}$, where L=NO, n=2; L=OH_2, NH_2R, etc., n=3; L=CN, n=4 are not well identified.[230] (Much of the published chemistry has not been done under controlled conditions, e.g. atmosphere, and so it is difficult to evaluate.) But if photolysis of an aqueous solution of nitroprusside initially generates $[Fe(CN)_5]^{3-}$ and NO^+,[238] then it is reasonable to suppose that if $[Fe(CN)_5NNAr]^{2+}$ were produced, it would be photosensitive, perhaps dissociating similarly.

b. Results and Discussion

Simply shaking a crystal of 4-methoxyaniline in a methanolic solution of sodium pentacyanonitrosylferrate(2-) in air and light gave rapid dissolution and a gradual color change to blue-green. This is comparable to the reaction in alkaline water solutions, which serves as a spot test for anilines.[239] Using equimolar quantities and monitoring the reaction by ultraviolet spectroscopy, a peak at ca. 488 nm grew in rapidly; equilibrium was attained in less than 0.4 h. A slower reaction occurred as well, building up peaks at 672 and 450 nm overnight in the dark. The lack of an isosbestic point, even in the first hour, indicates that these latter peaks may merely be obscuring the 488 nm and nitroprusside (498, 396 nm) absorptions.

Surprisingly, the deep blue solid product, precipitated from methanol by addition ~~of~~ ether, had an infrared spectrum characteristic of nitroprusside (ν(NO)= 1940, ν(CN)= 2140,2150,2170 cm^{-1}) but with some lower intensity absorption at 2100, 1500, 1380, 1250, 1170, 1020 and 840 cm^{-1}. The isolate would appear to be a mixture of nitroprusside with a small amount of intensely blue material. The reaction in methanol of 1:1:2 mole proportions of $Na_2[Fe(CN)_5NO]$, sodium acetate, and 4-methoxyaniline over 12 h in the dark gave very similar results. It appeared that the reaction was far from complete under these conditions. The poorer reactivity of anilines here compared to the primary alkylamines and ammonia used by Kenney[233] paralleled their reactivity in electophilic attack at metal carbonyls. (See section VI-A-2.)

In case the aniline/nitroprusside reaction was an equilibrium involving water and so capable of being displaced by driving off water (Equation VI-8), the reaction was carried out in refluxing absolute ethanol to allow removal of the ethanol/water azeotrope. There was no protection from light. This gave a reaction which, by the variety of colors of the solution at different stages, was obviously complex. $Na_2[Fe(CN)_5NO]\cdot H_2O$ alone reacted similarly, producing, after 1 day refluxing, a blue material nearly insoluble in alcohols, with a different UV spectrum from that of the products noted above. An infrared showed sharply reduced nitroprusside ν(NO) intensity and absorption at 2055 and 585 cm^{-1}. These are close to the values of $K_4[Fe(CN)_6]$.[240] The blue color would be expected from a salt with some Fe^{3+} cations, such as $NaFe[Fe(CN)_6]$.[241] Attempts to better define the product seemed unwarranted. It was clear that exchange of CN^- was occurring and that this was a poor choice of reaction conditions to obtain a diazenido complex.

Dehydration of $Na_2[Fe(CN)_5NO]\cdot H_2O$ was done without decomposition using benzene and distillation into a Dean-Stark still head. The dehydrated solid picks up water very readily. Benzene-azeotrope dehydration in the presence of an aniline gave slight reaction so that the solid was light grey, but the infrared was little affected so reaction was not appreciable, perhaps simply because of negligible solubility of sodium nitroprusside in benzene.

Another related route to a complex of $[(NC)_5FeNNAr]^{2-}$ could be synthesis of a hydrazine complex in the manner of Equation VI-6, with NH_3 replaced by $RNHNH_2$, and then oxidation of this to the diazenide (though agents such as H_2O_2 might react by initial substitution for hydrazine[242]). When synthesis of $[(NC)_5Fe(NH_2NHAr)]^{3-}$ was attempted by reaction under nitrogen in the dark of 1:2:4 mole proportions of $Na_2[Fe(CN)_5NO]$, sodium acetate and phenylhydrazine in methanol/water at 333 K,[233] a brown product formed overnight. This turned blue upon pouring in air, still in the dark, into cold ethanol. An infrared (yellow-green KBr suspension) of the solid product filtered from ethanol showed no $\nu(NO^+)$ and no indication of absorption due to a substituted phenyl ring. It appeared that the phenylhydrazine did attack the nitrosyl, but that $[Fe(CN)_5(NH_2NHPh)]^{3-}$, analogous to $[Fe(CN)_5(NH_3)]^{3-}$ (Eq. VI-6), did not collect at the hydrazine concentration used. Instead the phenylhydrazine dissociated to give the known[243] equilibrium mixture of $[Fe(CN)_5(OH_2)]^{3-}$ and $[Fe_2(CN)_5]^{6-}$. This was brown. Then pouring in air gave oxidation to the yellow-green $[Fe(CN)_5(OH_2)]^{2-}$ and blue $[Fe_2(CN)_5]^{4-}$.[244] The poor coordinating power of phenylhydrazine to pentacyanoferrate(II) is in agreement with the results of a kinetic study of the coordination of $NC_5H_4CONHNH_2$.[245] Therefore, this route was abandoned without further attempt to optimize reaction conditions to obtain $[Fe(CN)_5(NH_2NHPh)]^{3-}$.

c. Suggestion for Further Work

The most promising line to follow for synthesis of $Na_2[Fe(CN)_5(NNAr)]$ is suggested by the recent report of Nast and Schmidt.[231] They find that in liquid ammonia phenylimine anion does not reduce nitroprusside. Instead a nitrosoimine is obtained in moderately high yield (Eq. VI-3). This is reported to react with dilute aqueous acids, including water itself, to give violet solutions, and these we believe could contain $[(NC)_5FeNNPh]^{2-}$. Using nonaqueous acid it may well be possible to isolate the diazenide in good yield.

Similar chemistry in extremely basic media was reported long ago. An orange-yellow salt formed by reaction of nitroprusside and thiourea in methanol with excess methoxide and identified as $Na_5[(NC)_5FeN(O)NC(O)S]$ was hydrolyzed to a violet-red salt with analysis corresponding to Na:Fe:S:N of 3:1:1:7.[246] The diazenide alternative, $Na_3[(NC)_5FeNNC(O)S]\cdot H_2O$, to the previously proposed formulation of the red salt, $Na_3[(NC)_5FeN(O)NHC(O)SH]$, fits the analytic data equally well and in addition directly explains the slow decomposition of the red salt to dinitrogen. A partial duplication of this older work was recently reported. This is noteworthy because it contrasts the dark reactions (reaction at nitrosyl)[235] with light reactions (substitution for nitrosonium).[247]

Syntheses of aryldiazenidopentacyanoferrate(2-) complexes should be attempted by isolating nitrosoimine complexes prepared in very basic solution, then titrating with acid to allow displacement of the nitroso oxygen as hydroxide.

2. Other Metal Nitrosyl Complexes

a. Introduction

The electrophilic behavior of nitrosyl complexes[248] and the isoelectronic carbonyl or isocyanide complexes[163] has been the object of some consideration. The impression given by Angelici is that clear-cut differentiations of reactivity can be identified with the carboleptic systems. Force constants of MC–O stretching are a good indication of whether or not a complex has a sufficiently electrophilic carbonyl group. Reactions of electrophilic carbonyls are not complicated by competing electron transfer. And one type of product is obtained consistently from a given reaction. For instance metal carbonyls which react with primary alkylamines form carbamoyl complexes, never isocyanides. Angelici took little note of the variation in reactivity with different nucleophiles, though he mentioned that aromatic amines have not been found to act as nucleophiles.[163]

Nitrosyl chemistry is not so straightforward.

Eisenberg suggested that those metal nitrosyls with $\nu(NO)$ greater than about 1850 cm^{-1} are sufficiently electrophilic to be attacked.[249] Bottomley has proposed that nitrosyl complexes with $\nu(NO) \geq 1886$ cm^{-1}, $F(NO) > 1.38$ kN m^{-1} should show electrophilic behavior, but admitted that this measure is crude.[250] I believe this impression of imprecision arises for several reasons. First, Bottomley's study[250] covered a greater range of nucleophiles that Angelici's,[163] yet no regard was made for different reactivity of the nucleophiles. Second, Bottomley considered a broader range of nitrosyl complexes than Angelici did for carbonyl complexes. In particular, the list of nitrosyl complexes included species with charges ranging from 3+ to 2-. Though others do not comment on this point, it is at least interesting that the high ν(CO) complexes are cationic or polycarbonyls, whereas the high ν(NO) complexes are all mononitrosyls, and commonly anionic.

This brings us to the third point, the difference in bonding between that in high ν(CO) carbonyl and that in high ν(NO) nitrosyl complexes is sufficiently great that the correlation which works for the former is unlikely to work well for the latter. The problem of correlating (NO) with chemical properties was constructively discussed by Masek.[248] He pointed out that it is misleading to use ν(NO) to assign ligand (and thus metal) oxidation states by comparison with ν(NO) for NO$^+$, NO and NO$^-$, and then predict chemistry from these oxidation states. Furthermore it is virtually impossible, although Masek tried, to correlate ν(NO) with the chemical property of reduction potential because ν(NO) is quite insensitive to a variation in ligands which shifts the reduction potential by as much as 0.4 V. "It follows that the electron acceptance in the reduction is not localized exclusively on the NO group and that the redox orbital is a molecular orbital which is considerably delocalized over the whole molecule. An increase of the electron density on the central atom ... concerns of course much more this delocalized redox orbital than the π^*-MO on the NO group."[248] The nitrosyl stretching frequency may (or may not[251]) be a measure of electron structure about the ligand, but it is not a good measure of how readily a complex reacts with nucleophilic or reducing reagents.

To a greater extent than CO, coordination of NO^+ is accompanied by electron density shift to the ligand, because the nitrogen atomic orbitals are of lower energy than carbon. Added electron density as in a reduction goes therefore as much to the metal as the nitrosyl ligand. So the reduction potentials are sensitive to the state of the metal as well as the state of the ligand, as noted above. Furthermore, since reaction of hydoxide ion with coordinated nitrosyl "must be accompanied by a large electron density shift from the ligand to the central metal,"[248] this reaction is also sensitive to the state of the metal.

So to predict the feasibility of nucleophilic attack at a nitrosyl one requires a measure of ability of the metal to accept further electron density. To some extent this statement is trivial, since knowledge of some chemical property of a complex (E^o) is expected to be more helpful predicting a related chemical property than knowledge of a physical property (ν(NO)). But with this perspective it is reasonable that $[RuCl(das)_2NO]^{2+}$, F(NO)= 1.38 kN m^{-1}, could react with hydroxide though $[RuCl_5NO]^{2-}$, F(NO)=1.39 kN m^{-1}, does not.[250]

Ruthenium in the former cation with soft arsine ligands is understandably better able to absorb electron density from the nitrosyl during reaction with nucleophiles. To return to nitroprusside as an example, one can use these arguments to rationalize the greater reactivity with anilines of $[RuCl(bipy)_2NO]^{2+}$ compared to $[Fe(CN)_5NO]^{2-}$, even though infrared evidence suggests the opposite reactivity should obtain.

Table VI -1. Comparison of Properties of Nitrosyl Complexes

	$[RuCl(bipy)_2NO]^{2+}$	$[Fe(CN)_5NO]^{2-}$
ν(NO) in cm^{-1}	1927 [a] (1940 [b])	1938 [c]
F(NO) in kN m^{-1}	1.45 [c]	1.47 [c]
K_{eq} equation VII-1,2	1.6×10^9 [a]	1.5×10^6 [d]
E^o in V [e]	+0.20 [b]	-0.82 [f]

a) Ref. 252. b) Ref. 253. c) Ref. 250. d) Ref. 230.

e) In CH_3CN, vs. sat'd NaCl calomel. f) Ref. 236.

b. Results and Discussion

While the point is made that ν(NO) is a crude measure of electrophilic reactivity, it nevertheless remains useful. We tried to prepare $[IrCl_5NO]^-$, the complex with the highest reported value of ν(NO), for reaction with aniline and found it so electrophilic we were unable to work with it. And we found that other nitrosyls of lower ν(NO) were not active electrophiles.

Synthesis of $[IrX_5NO]^-$ has been reported by three groups, in 1963,[254] 1969,[255] and 1974.[251] Our work was done before the third paper was in press and like Bottomley's group[251] we could not prepare the nitrosyl by the older methods. The problem was principally that addition of nitrite salt to the strongly acid solution suggested in older literature quickly decomposed the nitrite without accomplishing nitrosylation. Our modification, heating $IrCl_6^{3-}$ in the presence of nitrite then adding concentrated aqueous HCl and evaporating with heating, was the same as Bottomley's but was not accomplished as successfully, perhaps because we did not boil off solvent before HCl addition. We were left with an impure brown solid after complete evaporation and lost $KIrCl_5NO$ during handling of a methanol extract. The other group obtained a precipitate of solvated $KIrX_5NO$ upon cooling the concentrated acidic solution.[251]

The electrophilic behavior of $[IrX_5NO]^-$ was reported in the paper with the latest communication of its synthesis.[251] The chloride complex is so electrophilic that it was impossible to obtain solution spectra of the nitrosyl complex free from nitro, $[IrCl_5NO_2]^{3-}$. The equilibrium constant for the reaction of

$$IrCl_5NO + 2\ OH \rightleftarrows IrCl_5NO_2{}^{3-} + H_2O \qquad \text{(VI -8)}$$

is $>6 \times 10^{29}$, close to that for free NO^+ and NO_2^-.[251] Most chemistry was tried with $IrBr_5NO^-$, in which the reactivity is sufficiently reduced to allow more definitive study. Even so, trials with an aniline did not give identifiable products.[256] It is reasonable that an Ir-NNAr complex would form but the Ir-N bond, like that in $[IrBr_5N_2]^{2-}$,[251] would be so weak that the complex would not survive in the reaction mixture. Thus we do not believe further work with this is warranted.

A similar example was recently reported. The product of reaction of NO with $MoCl_5$ has an infrared absorption assigned as νNO at 2000 cm^{-1}. Like $[IrCl_5NO]^-$ this material is so reactive it could not be manipulated. And reaction of this "red nitrosyl" with aniline gave uncharacterizable mixtures.[257]

The neutral complexes in the equilibrium

$$B(pz)_4Mo(CO)_2NO + ArNH_2 \rightleftarrows B(pz)_4Mo(CO)_2(NNAr) + H_2O \qquad \text{(VI -9)}$$

are both known and stable in solution,[61] so an attempt was made to displace the equilibrium to the right by removing the water produced. Refluxing a benzene solution of the nitrosyl with two moles 4-methoxyaniline overnight and collecting the vapor in a Dean-Stark trap was ineffective. The rate of attack of aniline at the nitrosyl is too slow to be useful. The N-O stretching frequency of 1665 cm^{-1} is well out of the range in which electrophilic character is expected.[250]

By its infrared ($\nu(NO)$=1867 cm^{-1}) the nitrosyl of $Fe(mnt)_2NO^-$ is borderline electrophilic. When $Et_4N[Fe(mnt)_2NO]$ and 4-methoxyaniline were mixed at room temperature in ethanenitrile, a new peak arose in the UV-visible spectrum at 442 nm. The infrared spectrum of the residue left upon evaporating the reaction mixture to dryness also indicated a reaction had occurred. The $\nu(NO)$ was shifted to 1835

cm^{-1} and ν_{symm}(COC) to 1250 from 1238 cm^{-1}; weaker absorptions appeared at 1780 and 1725 cm^{-1}. But in attempting to recrystallize this material from ethanenitrile/ether a decomposition occurred and only a salt of $[Fe(mnt)_2]_2^{2-}$ precipitated. (The dried filtrate absorbed weakly at 1835 cm^{-1}.) Running the reaction between 233 and 273 K and stripping the mixture while cold gave a nearly identical result except that i) the crude product had almost no nitrosyl absorption and ii) coordination of the amine to iron was apparent from the infrared, e.g. ν(NH) shifted from 3430, 3360, and 3230 in methoxyaniline down to 3300, 3250, and 3160 cm^{-1}, ν(NH) at 1630 broadened and lowered.

The bis(maleonitriledithiolate)nitrosylferrate (II) complex is apparently electrophilic, but more at the metal than at the nitrosyl. This result is not unexpected, for the diamagnetic iron is at least formally a 16-electron system, which could coordinate a nucleophile. The loss of nitrosyl, presumably as NO gas,[221] is also reasonable since this is in a sense just the reverse of the reaction by which the nitrosyl complex is formed.

$$[LFe(mnt)_2]^{n-} + NO \xrightleftharpoons[+L=NH_2Ar]{-L=Fe(mnt)_2^-} [FeNO(mnt)_2]^- \qquad (VI-10)$$

The nitrosyl is displaced from $FeNO(mnt)_2^-$ by pyridine.[221] While $FeNO(S_2C_6H_3Me)_2^-$ and complexes with other less electron-withdrawing dithiolates are more stable to nitrosyl loss,[221] they are also less likely to have a sufficiently electrophilic nitrosyl. Because our interest was in diazenido complexes, we did not pursue this sort of reaction further.

3. Summary and Prognosis.

In spite of the lack of any success in the work reported herein, this area should be further tested. It is clear from the literature that the reaction between a metal nitrosyl and an amine is a delicate balance. It requires an electrophilic complex, but one which reacts appreciably faster at the nitrosyl nitrogen than at the metal. It requires a nucleophilic amine, but not one that will act as a reducing agent.

The extremely electrophilic iridium complexes $[IrX_5NO]^-$ are not useful for they react with solvent or by electron transfer. The complex $B(pz)_4Mo(CO)_2NO$ and many others are simply not sufficiently reactive electrophiles. By the measure of nitrosyl stretching frequency, nitroprusside should react. Indeed, the complex does react with aminoalkanes and ammonia,[233] probably forming from ammonia an unstable dinitrogen complex, $[Fe(CN)_5N_2]^{3-}$. Similarly alkyldiazenides, $[Fe(CN)_5NNR]^{2-}$, could be present in equilibrium as intermediates from nitroprusside and amines. Such intermediates are destroyed by mild heating, allowing the amine coordination found in Kenney's products,

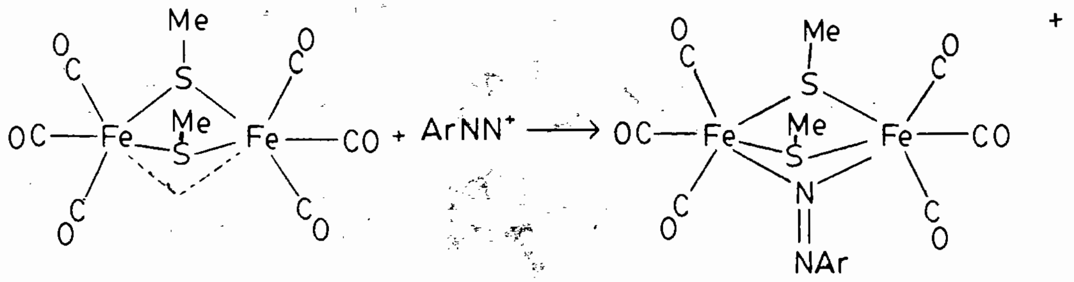
$$[(NC)_5FeNNR]^{2-} \xrightarrow{+\ RNH_2} [(NC)_5FeNH_2R]^{3-}.$$

A study of this reaction by UV or ir below temperatures of ready decomposition might be instructive, but only after isolation and characterization of [$(NC)_5FeNNR]^{2-}$ (See section VI -A-1-c.) so that its presence in reaction mixtures can be inferred more positively.

B. Reactions of Di- and Tri-nuclear Iron Carbonyl Complexes with Diazonium Tetrafluoroborates.

1. Introduction

One of the common synthetic methods used for aryldiazenide complexes is the substitution by $ArNN^+$ for a metal-bound carbonyl.[25] In our laboratory this was used to produce $[Fe(CO)_2(NNAr)(PPh_3)_2]BF_4$ from $Fe(CO)_3(PPh_3)_2$.[258] An intriguing extension of this method was to apply it to polynuclear carbonyls. We used $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $\{Fe(CO)_3SMe\}_2$. Such species are particularly interesting because they provide opportunity for an alternative reaction to substitution. Particularly in reference to the thiomethyl-bridged complex, we felt it was also possible for a diazonium salt to attack the metal-metal bond and add with no carbonyl being displaced, in a reaction such as the following.



However, the reactions we conducted produced no diazenide complexes.

2. Results and Discussion

4-Fluorobenzenediazonium ion appeared to react with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ by oxidizing a portion of the iron reactant, presumably to a salt such as $Fe(BF_4)_3$. The one-electron oxidation products of many transition metal carbonyl complexes are not stable and similarly decompose with evolution of carbon monoxide. No effort was made specifically to recover the organic product of the decomposition of the reduced diazonium salt. Diazonium salts have been known to react as one-electron oxidizing agents with other transition metal complexes.[193,259,260]

It was interesting that a reaction occurred in benzene between $Fe_2(CO)_9$ and a diazonium tetrafluoroborate since both species have negligible solubility. In this case it was the diazonium salt which reacted incompletely. Though $Fe_2(CO)_9$ was consumed, the product did not solidify to allow purification and identification. The low consumption of diazonium salt was not encouraging for the sort of syntheses we desired.

Although complete recovery of either reactant was not obtained, it is clear that there is no reaction between $\{Fe(CO)_3SMe\}_2$ and the diazonium salts used. The diazonium salts did not attack the bridging alkylthio sulfur (in contrast to the reactions of Chapter V) or oxidize the iron complex. Instead, they decomposed to organic products, especially at high temperatures, leaving the solution acidic. Iron complexes present in crude isolates were lost during workup, probably due to aerial oxidation, with a minor amount of reaction with diazonium decomposition intermediates possible.

3. Summary and Prognosis

There is no apparent reason for any further study of the reactions reported here. However this does not mean that slightly different approaches would not be productive. For instance, the bridged complex $\{Mn(CO)_4(NNPh)\}_2$ has been synthesized from phenyl(trimethylsilyl)diazene.[33] So it is possible to obtain a diazenide adduct of a metal carbonyl complex without stabilizing phosphine[261] or other ligands.

Furthermore, since the completion of our work several reports of electrophilic addition to metal-metal bonds have appeared. Insertion of diazonium into the metal-metal bond of $[\{Ir(NO)(PPh_3)\}_2O]$ [50] and $[\{PdCl(Ph_2PCH_2PPh_2)\}_2]$ [51] has shown that the reaction envisioned for the thiomethyl-bridged iron dimer is indeed possible. In light of this the protonation of the Fe-Fe bond in $\{Fe(CO)_2L(\mu\text{-}SMe)\}_2$ when L= $PMe_{3-n}Ph_n$ is quite encouraging.[262] It implies that the metal-metal bond in the tricarbonyl, which was not protonated, was just not sufficiently nucleophilic, since we have noted above (Chapter IV) that diazonium salts will react with complexes which can be protonated at the metal. It would be quite interesting to see how well this generalization extends to comparable formation of bridging hydride and diazenide complexes.

A closely related area of study is the formation of bridging aryldiazenide and nitrosyls by oxidative-additions not at a metal-metal bond. NO^+ oxidatively adds to the thiolate-bridged iron(II) dimer of N,N'-dimethyl-N,N'-bis(beta'-mercaptoethyl)ethylenediamine to form an Fe(III) dimer with a metal-metal bond and a bridging nitrosyl.[263] Elemental halogens add to $[L_3Mo(CO)_2(NNAr)]^{n+}$ (L_3 = $HB(pz)_3$, n=0;[264] L_3 = {(1,10-phenantholine)(PPh_3)}, {(2,2'-bipyridine)(PPh_3)}, n=1 [265]) to produce multiply bridged dimers $\{L_3Mo(\mu\text{-}X)_2(\mu\text{-}NNAr)_2\}_2$.

The immediate extension of our work would be to try the reaction of diazonium salts with the aforementioned $\{Fe(CO)_2L(-SMe)\}_2$.

4. Experimental

a. $Fe_3(CO)_{12}$

When solid $4\text{-}FC_6H_4N_2BF_4$ (36 mg, 0.17 mmole) was gradually added under argon to an intensely colored solution of $Fe_3(CO)_{12}$ (87 mg, 0.17 mmole) in 15 ml dichloromethane, there was no bubbling or other obvious evidence of reaction. The solution was stirred 0.8 h and filtered under argon. The golden brown solid was evidently $Fe(BF_4)_3$. Infrared spectrum: ν(BF) 1083 s, 1123 m; (4-F-aryl) 1485, 1255, 1230, 820 cm^{-1} vw. This solid was somewhat soluble in ater. Addition of sulfuric acid and KSCN to the water solution gave a red positive test for Fe(III) ions. The dark green dichloromethane filtrate did not separate at 259 K and so was concentrated to half volume and recooled. The black crystals which formed were collected and shown to be $Fe_3(CO)_{12}$ by comparison of their infrared spectrum (Nujol) with that of the reactant. No attempt was made to isolate other substances from the reaction.

b. $Fe_2(CO)_9$

In small portions solid $4\text{-}FC_6H_4N_2BF_4$ (56 mg, 0.26 mmole) was added with stirring to a suspension of orange $Fe_2(CO)_9$ (96 mg, 0.26 mmole) in 20 ml benzene in an aluminum-foil-wrapped flask. No immediate reaction could be detected. After stirring for 24 h the mixture was filtered. The vacuum dried, light tan solid was identified as (impure) $4\text{-}FC_6H_4NNBF_4$ by comparison of its infrared with that of known material. The brown impurity, insoluble in propanone or ethanenitrile, showed in the infrared only a broad absorption at 500 cm^{-1} and those at 3400 and 1625 cm^{-1} typical of water of hydration. The mass of diazonium salt filtered from the reaction mixture was 70% of that added. The benzene-soluble filtrate did not crystallize upon concentration. The dark scum left after removal of all solvent was soluble in ethanol. Infrared spectrum of a dilute KBr pellet: 2072, 2036, 2000 (br with unresolved sh at 1990), 1597, 1492, 1227, 1156, 860, 835, 610 cm^{-1}. There was no trace of a bridging νCO.

When this reaction was done in 30 ml ethanol under argon, one could see some tiny bubbles forming in solution after the solid diazonium salt had dissolved, especially with stirring briefly discontinued. There was no noticeable heating. After 0.5 h gas evolution could no longer be seen but solution color was just beginning to develop. (In a blank run without $Fe_2(CO)_9$ color developed in ethanol in 0.8 h.) Overnight the liquid became brown with a slight reddish cast, but insoluble orange crystals of $Fe_2(CO)_9$ were still suspended. When these were filtered off and all solvents from the filtrate, the solid residue had almost no infrared absorption other than that of BF_4. A qualitative test for iron with acidic thiocyanate was positive.

c. $\{Fe(CO)_3(\mu\text{-}SMe)\}_2$

After stirring for 2 h with an argon flush, a mixture of $\{Fe(CO)_3(SMe)\}_2$ (119 mg, 0.318 mmole), $4\text{-}FC_6H_4NNBF_4$ (133 mg, 0.636 mmole) and 20 ml benzene were allowed to stand in the dark 21 days and then filtered. By infrared the vacuum dried, deep red filtrate contained only $\{Fe(CO)_3(SMe)\}_2$ and so was not further investigated. The tan solid was separated into three portions: The propanone-insoluble portion was brown and gave a positive acidic-NCS^- test for Fe(III). It is a simple salt such as $Fe(BF_4)_3$ since an infrared of the crude solid had no absorption in the CO stretching region: 1000-900 vvbr, 400 cm^{-1} vvbr. A second substance was soluble in propanone and precipitated with ether; identified as $4\text{-}FC_6H_4NNBF_4$ by mp 167 (dec) and infrared. The unidentified material not precipitated by ether was characterized only by infrared: 1485 w, 1230 w, 1120 m, 1080 s, 820 w, 595 w, 530 w, 495 cm^{-1} w, all sharp. Essentially the same product distribution was obtained when these reactants were heated and stirred 6.7 h at 323 K, or refluxed two days under nitrogen.

Reaction of 4-$Et_2NC_6H_4NNBF_4$ under nitrogen in refluxing benzene gave after two days a brown insoluble solid and a green solution. The green solution had a composition closely related to the previous reaction: volatile $\{Fe(CO)_3(SMe)\}_2$, a slightly volatile white solid with prominent infrared bands (CCl_4) at 2980, 1615, ca. 1580, 1525, 1490, 1380, 1360, 1265, 1200, 1160, 1075, 1005, 980, and 695 cm^{-1}, and an involatile residue which contained no new iron-carbonyl complex. (IR: ca. 2500, νNH of $ArEt_2NH^+$; ca. 1050, νBF_4) The brown solid showed broad, intense νBF_4 at 1065 cm^{-1} and likely includes some simple iron tetrafluoroborate. The CO stretching region has two weak-medium, sharp bands at 2090 and 2040 cm^{-1}. The nature of the iron complex could not be investigated because it could not be isolated in a purer condition.

At room temperature in the dark an ethanolic solution of 4-$FC_6H_4NNBF_4$ (0.2 mmole) and $\{Fe(CO)_3(SMe)\}_2$ (0.1 mmole) decomposed in a week, leaving the iron dimer unchanged. Ultraviolet irradiation of a mixture of the same composition gave rapid loss of diazonium salt. Careful evaporation of ethanol gave crystallization of unreacted $\{Fe(CO)_3(SMe)\}_2$. Vacuum drying was acco{anied by sublimation of remaining iron dimer and left a product with carbonyl absorptions at 2100 and 2055 cm^{-1}. The M-CO region had peaks at

600, 570, 520 and 500(sh) cm^{-1}. The only other peaks were from water (3450, $1620\ cm^{-1}$ br) and BF_4 (1120sh, 1080, 1050sh cm^{-1}). The material did not crystallize.

C. Attempted Syntheses of Pentammine(phenyldiazenido)ruthenium Chloride.

1. Introduction

The first identified dinitrogen complex was $[Ru(NH_3)_5N_2]Cl_2$.[266] This simple complex is remarkably stable, particularly toward oxidation.[7] The electron-rich Ru(II) center seems to interact well with the orbitals of N_2, though the nature of the bonding is still in dispute.[267] A similar interaction occurs in pentammineruthenium(II) complexes with other π-acid ligands as well: NO, CO, NCR.[267a] We believed the synthesis of $[Ru(NH_3)_5(NNAr)]^{3+}$ would allow spectroscopic and chemical comparisons to be made with these simpler analogues, which in turn might allow a useful bonding picture for the aryldiazenide to be drawn. Furthermore $[Ru(NH_3)_5NNAr]^{3+}$ could have some interesting reaction chemistry.

Two routes to $[Ru(NH_3)_5NNAr]^{3+}$ were tried. The more rational one was replacement of labile water from $[Ru(NH_3)_5OH_2]^{2+}$ by diazonium ions. The other was modelled on syntheses of N_2 and NO complexes from N_2H_4[268] and NH_2OH.[269] Neither was successful.

2. Results

a. Reactions of Diazonium Salts with Ruthenium Ammines

There are few ligands which are cationic. The only two common examples with an overall formal positive charge at the coordinating function are nitrosyl and diazenide. There are no examples of nitrosonium or benzenediazonium coordinating to a positively charged metal complex, though Me_3S^+ [272] and H^+ have been known to do so, e.g.

$$Rh(NCMe)_2(dppe)^+ + H^+ \xrightarrow{MeCN} [HRh(NCMe)_3(dppe)]^{2+}.$$

Thus, the reaction is probably unknown because there are few potential examples, and these might have inherently high activation energies. In attempting one such reaction we found that $4\text{-}FC_6H_4NNBF_4$ and $[Ru(NH_3)_5OH_2]^{2+}$ formed an organic product, insoluble in the water solvent, tentatively identified as a mixture of 4,4'-difluorobiphenyl and bis(4-fluorophenyl)diazene. Infrared spectra indicated the presence in the product of the former, which was also obtained from reduction of 4-fluorobenzenediazonium salt with zinc amalgam. The latter product was previously unreported but the electronic spectra were clearly indicative of an azo compound. The presence of the azo compound suggested that there was some unusual mode of reaction between the ruthenium and the diazonium ion. However if any complex was produced it did not survive under the reaction conditions.

After these reactions had been done we learned of an earlier, brief Russian paper[273] reporting formation of

$[\{Ru(NH_3)_5\}_2N_2](BF_4)_4$ from diazonium salts and $[Ru(NH_3)_5OH_2]^{2+}$. The highly-charged dinitrogen-bridged dimer did not precipitate in our reactions and so presumably was not formed. The dimeric product almost certainly formed by combination of $[Ru(NH_3)_5NN]^{2+}$ with $[Ru(NH_3)_5]^{2+}$. $[Ru(NH_3)_5NN]^{2+}$ was found by us to be stable in methanol in the presence of benzenediazonium ion over a period of 2 hr. Over longer periods the ruthenium complex did decompose in solution.[79] The difference in products obtained between the Russian work and ours probably arose from having an excess of diazonium salt in our work and an excess of pentammineruthenium(II) in the other.[274] Our work concurs with this earlier report in finding no aryldiazenido product.

The fact that the dinuclear ruthenium complex forms by combination of two cations, while $[Ru(NH_3)_5NNAr]^{3+}$ does not, suggests that the diazo moieties of $(H_3N)_5RuNN^{2+}$ and $ArNN^+$ are not comparably bonded. We suggest that the former attacks $[Ru(NH_3)_5]^{2+}$ as a nucleophile, with electron density at the terminal nitrogen donated from the metal. (See Chapter I.) The postulated substitution of ethyl diazoacetate for water on $[Ru(NH_3)_5OH_2]^{2+}$ would be similar.[274] While there is formally a lone pair at the terminal nitrogen in a diazonium cation, $ArN\text{-}N{:}^+$, there is insufficient electron densZW for it to act as a nucleophile. $ArNN^+$ attacks metal complexes much as hydrogen ions would, as an electrophile. If, as was commonly assumed,[275] the initial bound state of dinitrogen in nitrogenase were well-modelled by the stable dinitrogen complexes such as

$[Ru(NH_3)_5N_2]^{2+}$, then reactions of diazonium salts[80] would be a poor indication of the potential mode of reaction of nitrogenase.

b. Reactions of Phenylhydrazine

Like two other groups,[276;79,256] we found that $RuCl_3$ and $[Ru(NH_3)_5Cl]Cl_2$ react with an excess of phenylhydrazine to produce $[Ru(NH_3)_5N_2]^{2+}$. In a preliminary run with one drop phenylhydrazine and an unmeasured quantity of aqueous $RuCl_3$ solution, a different brown solid precipitated. This was insoluble in ethanol and ether. From infrared evidence the phenyl moiety was definitely retained in the product. There was no band between 2100 and 1620 cm^{-1} and no other peak that suggested itself as νN=NPh. (This should be moderately intense in $[RuL_5NNPh]^{n+}$.[234]) So a bound diazenide was not isolated in any detectible quantity. The phenyl infrared absorptions are then most likely due to bound aniline.[277] The frequencies characteristic of ammonium ion (3150 s br, 1400 cm^{-1} m) are quite apparent and since the solid is water-insoluble, ammonium is almost certainly the counterion of an anionic ruthenium complex. A possible formulation is $NH_4[RuCl_3(NH_2Ph)_x(NH_3)_{3-x}]$ where x is the average number of coordinated anilines, close to three according to elemental analysis.

3. Prognosis

In summary, the reactions of phenylhydrazine with ruthenium(III) chloride and chlororuthenates were not productive. In order to improve the chances for isolation of pure solids with the aryldiazo ligands, reactions should be conducted in water rather than organic solvents, used in most of our trials. Other counterions, e.g. I^-, $ZnCl_4^{2-}$, and BPh_4^- might be investigated as well. Another reasonable way to synthesize the desired aryldiazenido complex would be to attempt synthesis of $[Ru(NH_3)_5NH_2NHAr]^{2+}$ and then oxidize this. Amine analogues of this hydrazine complex are known, and they are oxidized in air to isolable nitrile complexes,[278] or ~~to a~~ chelating imine[279] from $[Ru(NH_3)_4(NC_5H_4\text{-}2\text{-}CH_2NH_2)]^{2+}$.

4. Experimental

Zinc amalgam reacted with an aqueous solution of $4\text{-}FC_6H_4NNBF_4$ with vigorous gassing. After 2 min no further reaction was noticeable. The mercury was removed and methanol added. The electronic spectrum of the solution (266, 260 and 254 nm) agreed with that of C_6H_5F.[229] There was also a solid isolated, which was identified by comparison of its infrared spectrum with a reference spectrum[280]: 3080, 3040 vvw, 1605 m, 1510 s, 1230 s, 1160 s, 1085 m, 1015 wm, 835 s, 520 cm^{-1} w br.

Dissolution of $[Ru(NH_3)_5Cl]Cl_2$ (91 mg, 0.31 mmole) in 5 ml water occurred during reduction with amalgamated zinc over 0.5 hr. The presence of $[Ru(NH_3)_5OH_2]^{2+}$ was indicated qualitatively by the shoulder at 380-420 nm.[281] After removing the excess amalgam, the solution was added to the diazonium salt (65 mg, 0.31 mmole). A light brown suspension formed immediately, with darker insoluble material collecting more slowly (ca. 15 min). This mixture of coupled, organic compounds could be separated by centrifugation or filtering with fine porosity filter. It is at least partially volatile as it sublimed ~~during vac~~uum drying. Electronic spectrum in ethanol (λ_{max} in.nm): 430(sh), 325, 265(sh), 225(sh). Infrared spectrum in CCl_4 (4000-1120, 1000-825 cm^{-1}: ca. 3050 vvw, 1605 w, 1595 w, 1578 w, 1510 wm, 1500 wm, 1475 w, 1270 vw, 1235 wm, 1225 sh, 1185 wm, 1158 w, 1135 w, 835 wm. Addition to the filtrate of $NaBF_4$ (67 mg, 0.61 mmole) in a minimum amount of water did not precipitate a solid product, nor did addition of ethanol saturated with sodium chloride. After extracting with ether, which removed some additional organics similar to the water-insoluble material above, the solvents were all evaporated, leaving a red solid. The ethanenitrile soluble portion of this solid has infrared absorptions characteristic of $4\text{-}FC_6H_4NNBF_4$ with excess tetrafluoroborate. The insoluble is likewise identified as $[Ru(NH_3)_5Cl](BF_4)_xCl_{2-x}$. Anal. Found: C, 0; H, 3.59; N, 16.74. Calcd. for $[Ru(NH_3)_5Cl](BF_4)_2$: H, 3.82; H, 17.72. Infrared spectrum: ca. 3200 vvs br, ca. 2080 w br, 1615 vs br, 1300 vs, 1080 s, 800 s, 560 m, 530, 520 wm, 450 cm^{-1} m.

One drop of phenylhydrazine was added to a filtered aqueous solution of RuCl and a black solid formed immediately at the top of the test tube. With shaking, there was considerable foaming, and bubbling. The solid was centrifuged and washed with water, ethanol (in which solvent the solid bubbled further.), and ether. The olive-green mother liquor was discarded. The brown solid was vacuum dried. Anal. Found:

C, 39.4; H, 4.65; N, 13.9. Calcd. for "$NH_4[RuCl_3(NH_2Ph)_3]$": C, 42.8; H, 4.99; N, 11.10. Infrared spectrum: 3220 s sh, ca. 3150 s (νNH); 2100 vw (νNN impurity); 1600 m (arom. and δ NH); 1495 m (arom.); 1400 m (ammonium); ca. 1265 wm (ammine); 1150-1095 wm, 1070 sh, 1025 w, 800 w sh; 755 m, 690 m (phenyl); 540 cm^{-1} vw.

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