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WITH $[Ir(CO)Cl(PPh_3)_2]$ AND RELATED

COMPLEXES

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Reactions of Aryldiazonium Ions

with $[Ir(CO)Cl(PPh_3)_2]$ and

Related Complexes

by

Alan Blyth Gilchrist

L.R.I.C., Paisley College of Science and Technology,
Scotland, 1962

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EXAMINING COMMITTEE:

Chairman: B.L. Funt

D. Sutton, Senior Supervisor

L.K. Peterson

K.N. Slessor

F.W.B. Einstein

A.D. Allen, Professor
University of Toronto
Toronto, Ontario

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REACTIONS OF ARYLDIAZONIUM IONS WITH

[Ir(CO)Cl(PPh₃)₂] AND RELATED COMPLEXES

Author:

(signature)

ALAN BLYTH GILCHRIST

(name)

21/11/74

(date)

ABSTRACT

Reactions of Aryldiazonium Ions with

[Ir(CO)Cl(PPh$_3$)$_2$] and Related Complexes.

Variously-substituted aryldiazonium salts have been reacted under varying conditions with Vaska's complex, [Ir(CO)Cl(PPh$_3$)$_2$], $\underset{\sim}{1}$, and its analogues, [Ir(CO)A(P)$_2$] (for A = Cl, P = MePPh$_2$, Me$_2$PPh, PPh$_3$; for A = F, Br, I, OClO$_3$, P = PPh$_3$), but only for P = PPh$_3$ have nitrogen-containing complexes been isolated; these have been characterised by spectroscopic, physical and chemical means.

By allowing [Ir(CO)A(PPh$_3$)$_2$] and RC$_6$H$_4$N$_2$BF$_4$ to react in either benzene-ethanol or benzene-iso-propanol medium, two series of iridium(III) complexes have been isolated: a series of five-coordinate cationic aryltetrazene complexes, [Ir(CO)(PPh$_3$)$_2${N$_4$(C$_6$H$_4$R)$_2$}]BF$_4$, $\underset{\sim}{4}$ (R = H, p-F, -Cl, -Br, -CF$_3$, -OCH$_3$) and a series of six-coordinate cationic ortho-metalated aryldiimide complexes, [Ir(CO)A(PPh$_3$)$_2$(HNNC$_6$H$_3$R)]X, $\underset{\sim}{5}$ (for A = Cl, R = H, p-F, -Cl, -Br, -CH$_3$, -NO$_2$, -CF$_3$, o-F, -Cl, -Br, -NO$_2$, m-CH$_3$, -OCH$_3$, -Br, -Cl, -NO$_2$, -F, and X = BF$_4$; for A = F, I, Br, R = o-Br, and X = BF$_4$; for A = OClO$_3$, R = o-Br and X = ClO$_4$).

The aryldiimide complexes, $\underset{\sim}{5}$, have been demonstrated to undergo reversible deprotonation on treatment with base; by this means a molecular six-coordinate ortho-metalated arylazo complex, [·Ir(CO)Cl(PPh$_3$)$_2$(NNC$_6$H$_3$R)], $\underset{\sim}{6}$ (R = p-Br) has been isolated and characterised.

Hydrogenation of the azo-function of the complexes 4, 5 and 6 has been studied. Mild catalytic (Pd) reduction of 5 and 6 resulted in the analogous arylhydrazine complexes, $[Ir(CO)Cl(PPh_3)_2(NH_2NHC_6H_3R)]BF_4$, 7 (R = p-Br, o-Br, -Cl, -NH_2, m-Br) and $[Ir(CO)Cl(PPh_3)_2(NH_2NHC_6H_3R)]$, 9 (R = p-Br), respectively. Similar treatment of the aryltetrazene complex, 4, however, did not produce the analogous hydrazine complex, but appeared to result in loss of the bidentate tetrazene ligand with formation of a dihydrido iridium complex, tentatively formulated as $[Ir(CO)H_2(PPh_3)_2]BF_4$.

A series of six-coordinate molecular iridium(III) arylazo complexes, $[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$, 8 (R = H, p-F, -Br, -OCH_3, o-F, m-NO_2) has been synthesised by allowing Vaska's complex (1), $RC_6H_4N_2BF_4$ and LiCl to react in acetone solution. Evidence has been presented that the arylazo ligand (ArN_2) in these complexes can be formulated as ArN_2^- rather than ArN_2^+. In keeping with this formulation, protonation of 8 to yield the cationic aryldiimide complex, $[Ir(CO)Cl_2(PPh_3)_2(HNNC_6H_4R)]BF_4$, 11 (R = p-F) occurs on treatment with HBF_4 in diethyl ether solution. The removal of a chloride ligand from 8 by reaction with AgBF_4 did not allow isolation of the anticipated five-coordinate arylazo complex, $[Ir(CO)Cl(PPh_3)_2(NNC_6H_4R)]BF_4$, 2, affording instead Vaska's complex (1) and $RC_6H_4N_2BF_4$, considered to be a result of the disproportionation of 2 in solution.

Owing to the unexpected nature of the products 4 and 5 arising from the reaction between [Ir(CO)A(PPh$_3$)$_2$] and RC$_6$H$_4$N$_2$BF$_4$ in benzene-ethanol or benzene-iso-propanol medium, the mechanism of this reaction has been investigated and, from the experimental data available, tentative mechanistic routes suggested.

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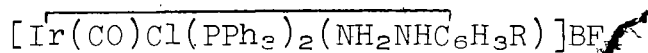with some of the experimental work.

Further, I am particularly indebted to
Merrily Dominelli and Marilyn Cheveldayoff
for so competently typing this thesis.
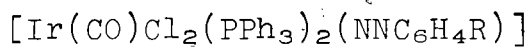
List of Numbered Compounds

Compound	Number
$[Ir(CO)Cl(PPh_3)_2]$	1
$[Ir(CO)Cl(PPh_3)_2(NNC_6H_4R)]BF_4$	2, R=p-F; o-F.
$[Ir(CO)Cl(PPh_3)_2(NO)]BF_4$ [22,23]	3
$[IrCO(PPh_3)_2\{N_4(C_6H_4R)_2\}]BF_4$	4a, R=H b, R=p-F c, R=p-Cl d, R=p-Br e, R=p-CF$_3$ f, R=p-OCH$_3$
$[Ir(CO)Cl(PPh_3)_2(NHNC_6H_3R)]BF_4$	5a, R=H b, R=p-F c, R=p-Cl d, R=p-CH$_3$ e, R=p-Br f, R=p-NO$_2$ g, R=p-CF$_3$ h, R=o-F i, R=o-Cl j, R=o-Br k, R=o-NO$_2$ l, R=m-CH$_3$ m, R=m-OCH$_3$ n, R=m-Br o, R=m-Cl p, R=m-NO$_2$ q, R=m-F
$[Ir(CO)A(PPh_3)_2(NHNC_6H_3o-Br)]BF_4$	5r, A=F s, A=I t, A=Br
$[Ir(CO)(OClO_3)(PPh_3)_2(NHNC_6H_3o-Br)]ClO_4$	5u
$[Ir(CO)Cl(PPh_3)_2(NNC_6H_3p-Br)]$	6

Compound	Number
$[Ir(CO)Cl(PPh_3)_2(NH_2NHC_6H_3R)]BF_4$	7a, R=p-Br
	b, R=o-Br
	c, R=m-Br
	d, R=o-Cl
	e, R=o-NH$_2$
$[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$	8a, R=H
	b, R=p-F
	c, R=p-Br
	d, R=p-OCH$_3$
	e, R=o-F
	f, R=m-NO$_2$
$[Ir(CO)Cl(PPh_3)_2(NH_2NHC_6H_3p-Br)]\cdot(C_2H_5)_2O$	9
$[Ir(CO)H_2(PPh_3)_2]BF_4$[a]	10
$[Ir(CO)Cl_2(PPh_3)_2(HNNC_6H_4p-F)]BF_4$	11

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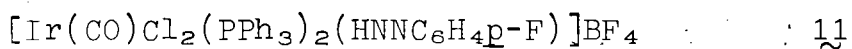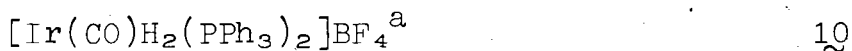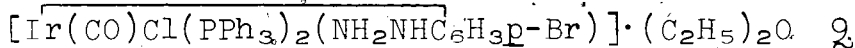
a. Tentative formulation

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CHAPTER 1

Introduction

The original aim of this work was to study the behaviour, not only of Vaska's complex[1], $[IrCl(CO)(PPh_3)_2]$ (1), trans-chlorocarbonylbis (triphenylphosphine) iridium(I) and its analogues, but also of other transition-metal complexes towards the aryldiazonium cation, ArN_2^+. It was hoped that such reactions would lead to the formation of arylazo complexes, two of which had already been reported by King[2,3] $([(h^5-C_5H_5)Mo(CO)_2(N_2Ar)])$ and Parshall[4-6] $([PtCl(PEt_3)_2(N_2Ar)])$.

The main interest in such complexes centred on the proposal by Parshall[5-7] that transition-metal arylazo complexes could be considered as possible models for the enzymatic fixation of molecular nitrogen (dinitrogen) occurring in certain plants and algae and by which atmospheric nitrogen is rapidly and quantitatively converted to ammonia under ambient conditions. Several review articles[8-16,28] on both the biological and chemical aspects of nitrogen fixation have appeared recently. It is quite clear that a basic requirement for the function of the enzyme, nitrogenase, in this process is the presence of both iron and molybdenum. One currently popular proposal[5,7,12,14,29], albeit lacking substantial proof (such as the isolation of dinitrogen, diimide or hydrazine complexes from the biological

system), is that one or both of the transition metals bind(s) the molecular nitrogen, thus reducing the bond order of dinitrogen and facilitating its reductive cleavage. On this basis, two of the pathways which have been suggested are outlined in Schemes 1[1] and 2[7,29] in which M and M' represent the enzyme-bound iron or molybdenum:

$$M \quad M' + N_2 \rightarrow M^{\diagup N \equiv N \diagdown}_{}M' \rightarrow M^{\diagup N = N \diagdown}M'$$

$$\xrightarrow{\text{H-Donor}} M-NH_2 \quad H_2N-M' \xrightarrow{\text{H-Donor}} M \quad M' + 2NH_3$$

Scheme 1

$$N \equiv N + \overset{+}{M'}$$
$$\overset{+}{\downarrow}$$
$$M-H \quad N \equiv N-M' \rightarrow M-\overset{H}{\underset{}{N}} = N-M' \xrightarrow[2e^-]{2H^+} M-\overset{H}{\underset{H}{\overset{+}{N}}}-\overset{H}{\underset{}{N}}-M'$$

$$\xrightarrow[2e^-]{2H^+} M-NH_2 + H_3\overset{+}{N}-M'$$
$$\Big\downarrow \begin{matrix}2H^+\\2e^-\end{matrix} \qquad \Big\downarrow$$
$$M-H + NH_3 \qquad \overset{+}{M'} + NH_3$$

Scheme 2

Among the chemical models suggested for the biological reduction of dinitrogen are those involving dinitrogen complexes and arylazo complexes of transition metals. A variety of stable terminal-dinitrogen (c.f., Scheme 2) and bridging-dinitrogen (c.f., Scheme 1) complexes have been prepared, but none has proved capable of reduction to ammonia[13,18-21].

In support of scheme 2, Parshall[4-6] reacted the platinum hydride [PtClH(PEt$_3$)$_2$] (representing M-H) with an aryldiazonium cation N$\equiv\overset{+}{N}$-Ar (representing N$\equiv\overset{+}{N}$-M'). The initial product, [PtCl(HN=NAr)(PEt$_3$)$_2$], is an analogue of the diimide complex postulated as an intermediate in Scheme 2 and can be reduced by platinum-activated hydrogen under prolonged conditions to ammonia, via the arylhydrazine complex, [PtCl(H$_2$NHNAr)(PEt$_3$)$_2$]$^+$ which resembles another of the proposed intermediates in the biological system[7].

As indicated earlier, it was intended in this work to prepare a series of arylazo complexes in which not only the ligands on the metal and the substituents on the ring of the arylazo unit would be varied, but also the metal itself; in this way the electronic environment around the azo (-N=N-) function could perhaps also be varied, and the ease of its reduction related to the change in the (N=N) bond order. However, the scope afforded by the reaction of only Vaska's complex (1) and its analogues with variously substituted

aryldiazonium cations was such as to preclude, as part of this thesis, further work involving other transition metals.

The choice of Vaska's complex, $[IrCl(CO)(PPh_3)_2]$ ($\underset{\sim}{1}$), as the first candidate for reaction with aryldiazonium cations was based on the premise that the resulting product would be the five-coordinate cationic arylazo adduct $[IrCl(CO)(N_2Ar)(PPh_3)_2]^+$ ($\underset{\sim}{2}$), analogous to the known nitrosyl complex $[IrCl(CO)NO(PPh_3)_2]^+$ ($\underset{\sim}{3}$)[22,23].

Vaska's complex ($\underset{\sim}{1}$), a square-planar d^8 complex, is both electronically and coordinatively unsaturated and had already been shown to readily undergo a large number of oxidative addition reactions[24-27]. Thus, it readily reacts with nitrosonium tetrafluoroborate, $NO^+BF_4^-$, yielding the iridium(III) nitrosyl complex ($\underset{\sim}{3}$). The aryldiazonium cation, $Ar-\overset{+}{N}\equiv N$, can be considered to be isoelectronic with NO^+, and could be expected to yield the arylazo complex ($\underset{\sim}{2}$) on reaction with Vaska's complex ($\underset{\sim}{1}$).

The nitrosyl complex ($\underset{\sim}{3}$) afforded the first example (and the only one at the onset of this work) of a nitrosyl complex with a bent M-N-O moiety[22,23]. It was thus of great interest, in this sense, to achieve the synthesis of the analogous arylazo complex ($\underset{\sim}{2}$) and to ascertain the nature of the bonding of the arylazo ligand to the central metal.

As it transpired, synthesis of the anticipated product ($\underset{\sim}{2}$) by this route was not achieved; instead two entirely

unexpected complexes, a five-coordinate cationic iridium(III) aryltetrazene complex, [IrCO(N$_4$Ar$_2$)(PPh$_3$)$_2$]BF$_4$ (4), and a six-coordinate cationic iridium(III) ortho-metalated aryldiimide complex, [IrCl(CO)(HNNAr)(PPh$_3$)$_2$]BF$_4$ (5), were isolated from the reaction between Vaska's complex (1) and the aryldiazonium tetrafluoroborate salts, ArN$_2$BF$_4$.

This failure to obtain the five-coordinate arylazo complex (2), and the unanticipated isolation of the obviously interesting complexes (4) and (5), prompted a change in the original aim of this thesis to an emphasis on the extent to which these compounds could be obtained and characterised for a variety of ligands and substituents. Thus, a series of the aryltetrazene complexes (4), and a series of the aryldiimide complexes [IrA(CO)(HNNAr)(PPh$_3$)$_2$] Y (5) have been prepared and characterised. These are discussed in Chapters II and III, respectively.

Treatment of the aryldiimide complexes (5) with base results in the six-coordinate molecular ortho-metalated arylazo complexes, [Ir A (CO)(N$_2$Ar)(PPh$_3$)$_2$] (6), which are discussed in Chapter IV.

On hydrogenation in the presence of a palladium catalyst at room-temperature, the aryldiimide complexes (5) are converted to the arylhydrazine complexes, [IrCl(CO)(H$_2$NHNAr)(PPh$_3$)$_2$]BF$_4$ (7). These are discussed in Chapter V, along with the hydrogenation studies on the complexes (4) and (6).

Failure to isolate the five-coordinate arylazo complex (2) suggested that it might be unstable, particularly with respect to ortho-metalation as the six-coordinate diimide complex (5), which could result from ortho-metalation of the arylazo ring in (2), is a stable, isolable species. Thus, reactions between Vaska's complex (1), and aryldiazonium cations were performed in the presence of chloride ion to block the sixth coordination position of the iridium and to prevent ortho-metalation. When these reactions were performed in benzene-ethanol or benzene-isopropanol media, i.e., in the same media as required to yield the aryltetrazene (4) and aryldiimide complexes (5), the anticipated six-coordinate molecular arylazo iridium(III) complexes $[IrCl_2(CO)(N_2Ar)(PPh_3)_2]$ (8) were not obtained. However, when the reactions were carried out in acetone medium the complexes (8) were successfully isolated and characterised; they are discussed in Chapter VI.

The unexpected formation of both an aryltetrazene complex (4) and an aryldiimide complex (5) from the reaction between Vaska's complex (1) and an aryldiazonium cation, ArN_2^+, poses an intriguing problem as to the nature of the mechanistic route leading to these two complexes. The results of the work done in an attempt to elucidate the mechanism are presented in Chapter VII.

In summary, the study in this thesis, deviating from the original aim to investigate the ease of reduction of the azo (-N=N-) function in a variety of transition metal complexes, centres mainly on the two novel classes of iridium complexes, (4) and (5), isolated from the reaction between Vaska's complex (1) and the aryldiazonium cation, ArN_2^+, in either benzene-ethanol or benzene-isopropanol medium.

CHAPTER II

Cationic Aryltetrazene Complexes

A. Introduction

The term "tetrazene complex" as used here requires some clarification. The bidentate tetra-azadiene ligand, R-N=N-N=N-R, can probably bond to a metal in at least two ways[30-35] as represented by Fig. II-1(a), a 1,4-disubstituted tetrazene complex, and Fig. II-1(b), a 1,4-disubstituted tetra-azadiene complex.

```
        N=N
       /    \
  R-N         N-R
       \    /
         M

        (a)
```

```
        N-N
      //    \\
  R-N         N-R
      \       /
        ↘ M ↙

        (b)
```
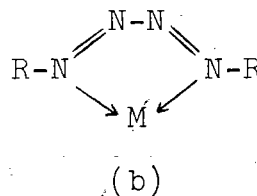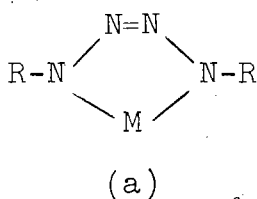
Fig. II-1

In this thesis, "tetrazene complex" is used as a general term applied to any 1,4- R_2N_4 complex, irrespective of the mode of bonding; the complexes 4a-f (see Table II-2) in which R is always aryl (Ar), and in which the bonding is closer to type 1(a) are referred to as aryltetrazene complexes.

It is of interest to note here that no examples of a free tetra-azadiene, R-N=N-N=N-R, are known and the tetrazene complexes thus represent a unique example of stabilization by

complex formation.

Few transition metal tetrazene complexes are known, and those which have been prepared and characterised were obtained by the reaction between a transition metal complex and an organic azide. The known tetrazene complexes and their preparations are listed in Table II-1.

The work presented here provides not only the first example of a cationic tetrazene complex, but also the first example of the synthesis of a tetrazene complex by a route other than via azides.

As will be discussed in detail in Chapter II C, the X-ray structural data for 4b favours bonding closer to the tetrazene type (Fig. II-1a) rather than the tetra-azadiene type (Fig. II-1b). Figure II-2 represents the general structure of the aryltetrazene cations, 4a-f

$$RH_4C_6-N \underset{OC}{\overset{N=N}{\diagup}} \overset{N-C_6H_4R}{\underset{Ir}{\diagdown}} PPh_3$$
$$PPh_3$$
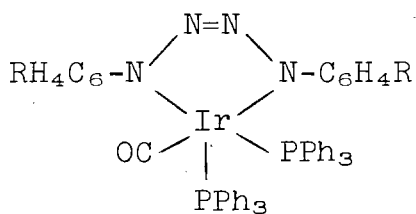
Fig. II-2

4a, R=H
b, R=p-F
c, R=p-Cl
d, R=p-Br
e, R=p-CF_3
f, R=p-OCH_3

Table II-1

Transition Metal Tetrazene Complexes

Complex	Preparation	Reference
$[Fe(CO)_3(N_4Me_2)]$	$MeN_3 + [Fe_2(CO)_9]$	30,31
$[Co(h^5-C_5H_5)(N_4R_2)]$ R = Me, Ph	$RN_3 + [(h^5-C_5H_5)Co(CO)_2]$	32
$[Ni(1,5-C_8H_{12})\{N_4(C_6F_5)_2\}]$[a]	$C_6F_5N_3 + [Ni(1,5-C_8H_{12})_2]$	33
$[NiL_2\{N_4(C_6F_5)_2\}]$[b]	$[Ni(1,5-C_8H_{12})\{N_4(C_6F_5)_2\}]+L$	33
$[M(NO)(PPh_3)(N_4R_2)]$ M = Rh, Ir R = $SO_2C_6H_4CH_3$	$RN_3 + [M(NO)(PPh_3)_3]$	36
$[M(NO)(PPh_3)L(N_4R_2)]$ M = Rh, Ir ; L = PPh_3, CO R = $SO_2C_6H_4CH_3$	$[M(NO)(PPh_3)(N_4R_2)]+L$	36
$[Pt(PPh_3)_2(N_4R_2)]$ R = $SO_2C_6H_4CH_3$, $SO_2C_6H_5$	$RN_3 + [Pt(PPh_3)_3]$	37,36
$[Ir(CO)(PPh_3)_2\{N_4(C_6H_4R)_2\}]BF_4$ R = H, p-F, Cl, Br, CF_3, OCH_3	$[RC_6H_4N_2BF_4+IrCl(CO)(PPh_3)_2$	This work

a $1,5-C_8H_{12}$ = cyclo-octa-1,5-diene

b   L = PPh_3, $MePPh_2$, Me_2PPh, $P(OMe)_3$; L_2 = bipyridyl

B. Synthesis

The aryltetrazene complexes, 4a-f, were readily prepared by the addition of the requisite aryldiazonium tetrafluoroborate, ArN_2BF_4, and ethanol (or iso-propanol) to a benzene solution of 1. The mole ratio of ArN_2BF_4 to 1 was held at 1:1. Although the apparent stoichiometry requires two moles of ArN_2BF_4 per iridium atom, this did not prove beneficial in practice: no improvement in yield resulted, the product was contaminated with a persistent small amount of diazonium salt, and some unreacted diazonium salt (ca. 15%) was recovered. In fact, no improvement over the 1:1 ratio of reagents was achieved by varying the ratio through a 100% excess of ArN_2BF_4 to a 50% excess of 1.

The ratio of alcohol to benzene was fixed at 1:10 (V:V). With this ratio, the aryltetrazene complex generally crystallised out on cooling or slow evaporation, whereas with a higher alcohol content (as used where isolation of the aryldiimide complex is required) crystallisation of the aryltetrazene complex did not occur, a more involved isolation procedure was required, and loss of aryltetrazene complex resulted.

In addition to the complexes, 4a-f, successfully isolated and characterised, as listed in Table II-2, attempts to isolate other variously substituted aryltetrazene complexes were unsuccessful. When the synthesis was attempted with the

Table II-2

Elemental Analyses, Decomposition Temperatures
and Yields for the Aryltetrazene Complexes,
$[Ir(CO)\{N_4(C_6H_4R)_2\}(PPh_3)_2]BF_4$ (4a-f)

Compound (R)	Percentage Composition						Decomposition Temperature[h] °C	Yield,[a] %	
	Found			Calculated				I[b]	S[c]
	C	H	N	C	H	N			
4a (H)	56.83	4.13	5.28	56.50	3.89	5.38	180	15	21
4b (p-F)[d],[e]	54.96	3.80	5.30	57.16	3.85	4.85	150	45	50
4c (p-Cl)[f]	52.80	3.45	5.27	53.03	3.46	5.05	150	23	50
4d (p-Br)[g]	49.84	3.59	4.44	49.66	3.54	4.45	125	25	43
4e (p-CF₃)	51.99	3.67	4.56	52.00	3.30	4.75		7	80
4f (p-OCH₃)	55.36	4.06	4.87	55.60	4.03	5.10	140	<10	15

(a) Based on a stoichiometry of 1 mole 1 + 1 mole $ArN_2^+ \to 0.5$ mole 4

(b) Percentage yield of pure, isolated compound.

(c) Percentage yield of product formed in solution during reaction, and calculated from the molar absortivities, $\epsilon_{500\ nm}$ (c.f., Chapter II, D4).

(d) Formulated with 1 mole C_6H_6 per 1 mole of complex; unable to obtain accurate carbon analysis, probably due to varying benzene of crystallisation.

(e) Fluorine (F) analysis: Found 9.56% ; Calculated 9.87%
     Phosphorus (P) analysis: Found 5.10% ; Calculated 5.36%

(f) Fluorine (F) analysis: Found 6.89% ; Calculated 6.85%.

(g) Formulated with 1 mole $(CH_3)_2CO$ per 1 mole of complex

(h) Temperature at which evidence of decomposition first appeared; determined using a Fisher Johns Melting Point Apparatus.

para-diethylamino and para-hydroxy phenyldiazonium cations, no evidence of aryltetrazene complex formation was observed and substantial amounts of unreacted 1 and ArN_2BF_4 were recovered (ca. 70% for the reaction with $Et_2NC_6H_4N_2BF_4$). It is obvious that electron-donor substituents on the aryl ring hinder the formation of the aryltetrazene complexes, and this is further indicated by the fact that of those reactions which did yield isolable aryltetrazene complexes, only in the para-methoxy case, 4a, was unreacted diazonium salt recovered (ca. 10%).

Although the use of both ortho- and meta-F,Cl,Br,NO_2,CH_3 and OCH_3-substituted phenyldiazonium cations did not permit the actual isolation of the aryltetrazene complexes, evidence for their formation was afforded by their electronic spectra (c.f. Chapter II D4) and the red colour of the reaction solution. However, when aryldiazonium cations substituted in both ortho-positions with (a) F, (b) Cl, and (c) CH_3, were used, no evidence for aryltetrazene complex formation was observed at all. This is attributed to steric interference at the nitrogen atom attached to the ring, thus preventing its approach to the iridium atom.

C. Structure

A single crystal X-ray structure analysis[34,35] of the red, crystalline p-fluoro compound, carbonylbis(triphenylphosphine) (1,4-p-fluorophenyltetrazene)iridium tetrafluoroborate (4b)

Interatomic Distances (Å)

Ir	–	P(1)	2.340 (4)	C(11)	– C(12)	1.379 (20)
Ir	–	P(2)	2.383 (4)	C(12)	– C(13)	1.389 (22)
Ir	–	C(1)	1.806 (13)	C(13)	– C(14)	1.352 (23)
Ir	–	N(1)	1.941 (10)	C(14)	– C(15)	1.352 (23)
Ir	–	N(2)	1.977 (?)	C(15)	– C(16)	1.307 (22)
P(1)	–	C(21)	1.829 (16)	C(16)	– C(11)	1.394 (21)
P(1)	–	C(41)	1.811 (16)	C(21)	– C(22)	1.421 (23)
P(1)	–	C(51)	1.796 (16)	C(22)	– C(23)	1.418 (24)
P(2)	–	C(61)	1.820 (16)	C(23)	– C(24)	1.375 (25)
P(2)	–	C(71)	1.834 (16)	C(24)	– C(25)	1.289 (24)
P(2)	–	C(81)	1.815 (16)	C(25)	– C(26)	1.393 (24)
C(1)	–	O(1)	1.166 (16)	C(26)	– C(21)	1.574 (22)
N(1)	–	N(3)	1.400 (18)			
N(1)	–	C(11)	1.481 (18)			
N(2)	–	N(4)	1.350 (16)	avg C – C (phenyl groups[a]	1.382 (4)[c]
N(3)	–	C(21)	1.456 (18)		
N(4)	–	C(24)	1.270 (19)	avg C – C (benzene)	1.368 (14)[c]
F(1)	–	C(14)	1.397 (19)		
F(2)	–	C(24)	1.381 (21)		
B(1)	–	F(11)	1.330 (30)[b]		
B(1)	–	F(12)	1.317 (20)[b]		
B(1)	–	F(13)	1.295 (20)[b]		
B(1)	–	F(14)	1.426 (29)		

a triphenyl phosphine groups

b uncorrected for riding motion; corrected values are 1.380 (F(11)) 1.406 (F(12)) and 1.396 (F(13))

c errors calculated form the formula

$$1/\sigma^2_{av} = \sum_{i=1}^{n} 1/\sigma^2_i$$
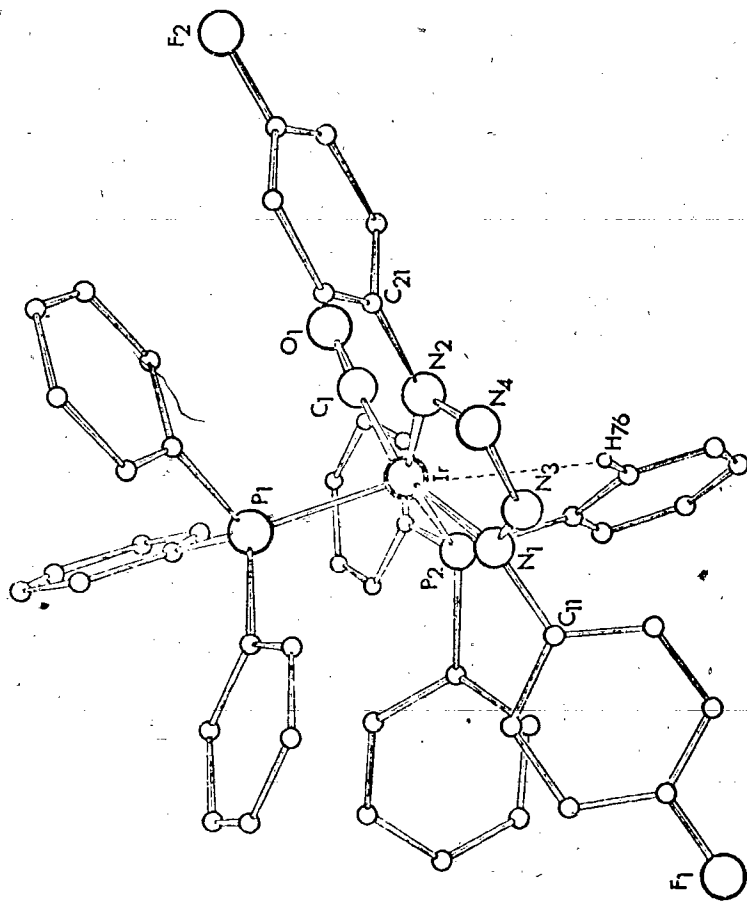
Diagram II-1. Molecular configuration of $[Ir(CO)(PPh_3)_2\{N_4(C_6H_4 \underline{p}\text{-}F)_2\}]^+$, 4b

showed the structure to consist of discrete pentacoordinate
iridium complex cations and tetrafluoroborate anions together
with benzene molecules of crystallisation (one benzene mole-
cule per iridium atom). The molecular configuration of the
cation is shown in Diagram II-1. The environment of Ir is
quite irregular but is closer to square-pyramidal geometry
with P(1) as apex and N(1), N(2), C(1) and P(2) as basal atoms;
these four atoms are not, however, coplanar.

The significant feature of the complex cation is the
presence of the five-membered iridium-nitrogen heterocycle.
The four nitrogen atoms are coplanar and the iridium atom is
displaced only 0.095 $\overset{o}{A}$ out of this plane towards P(1). The
N(3)-N(4) bond is significantly shorter than both the N(1)-N(3)
and N(2)-N(4) bonds. The short N(3)-N(4) bond indicates a
formal valence structure as depicted in Figure II-3a, rather
than the tetraazadiene ligand formalism shown in Figure II-3b.
Thus, the iridium, which is formally in an Ir^{III} (d^6) oxidation
state, is essentially σ-bonded to the 1- and 4-nitrogens. This
is in contrast to the iron complex $[Fe(Me_2N_4)(CO)_3]$[30] for which
X-ray crystallographic studies[31] indicate that the azadiene is
bonded to the metal via coordinate bonds from the 1- and 4-
nitrogens (Figure II-3c). As stated by La Monica et al[36] with
respect to their nitrosyltetrazene derivatives
$[M(NO)(PPh_3)_3(N_4R_2)]$(M = Rh, Ir; R = $SO_2C_6H_4CH_3$), it is diffi-
cult to describe the oxidation state of the metal in tetrazene
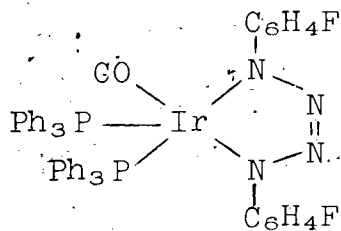
(a)
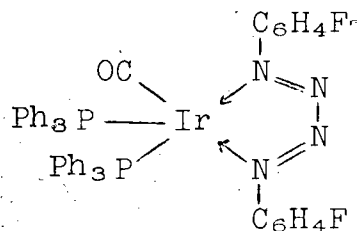
(b)
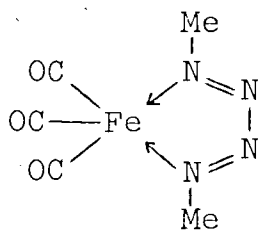
(c)
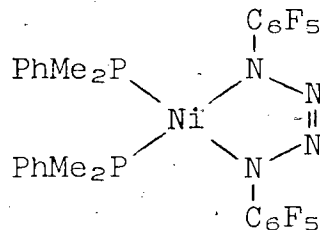
(d)
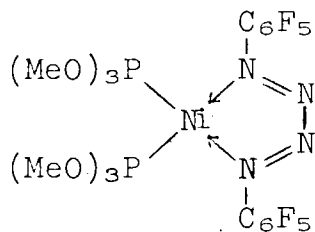
(e)

Figure II-3

derivatives because the organic moiety can be considered either as a bis-σ-ligand or as a ligand forming two-electron dative bonds from the 1,4 positions of the tetraazadiene group. For a series of Ni complexes having a coordinated tetraazadiene ligand, $[Ni\{(C_6F_5)_2N_4\}L_2]$ (L = PPh_3, PPh_2Me, $PPhMe_2$ or $P(OMe)_3$ and L_2 = bipyridyl, $1,5-C_8H_{12}$)[33], it is suggested that either of the two structural types in which nickel is either d^8 or d^{10} can exist, the presence of good σ-donor and poor π-acceptor ligands favouring the σ-bonded d^8 tetrazene structure (Figure II-3d), and good π-acceptor ligands favouring the d^{10} tetraazadiene structure (Figure II-3e).

The tetrazene structure in Figure II-3a for the iridium complex is further supported by the fact that the aromatic rings are neither coplanar with each other nor with the four nitrogen atoms; the conjugated π-system in Figure II-3b should result in a near planar configuration. Although the atoms C(11), N(1), N(2), N(3), N(4) and C(21) (Diagram II-1) are not strictly coplanar, the departure from coplanarity is much less than would be expected if the N(1) and N(2) lone pairs of electrons are localised. Delocalisation of these electron pairs is of importance, and there is a striking similarity between this heterocyclic ring and that of the tetrazolium salts[45] (Fig.II-4) and the tetrazaborolines[183] (Fig. II-5). The N(1)-N(3) and N(2)-N(4) bond lengths of 1.400(16) and 1.350(16)Å indicate essentially single bonds, whereas the Ir-N(1) and Ir-N(2) bond

lengths of 1.941(13) and 1.971(10)Å represent the lower extreme

of the range (1.95 - 2.15Å) suggested by Ibers and coworkers

for M-N single bonds[47]. The overall geometry, therefore,

justifies the representation of this complex ion as an iridio-

2,5-di-p-fluorophenyltetrazolium ion (Fig. II-6).
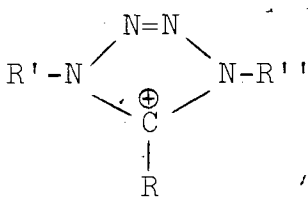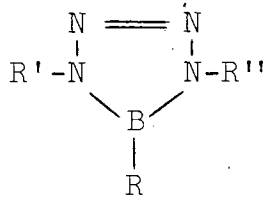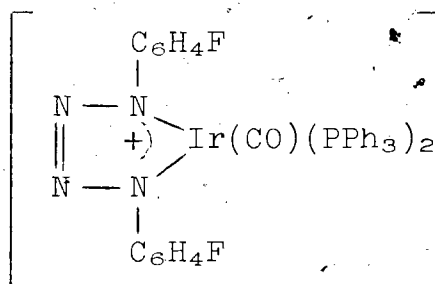
Fig. II-4   Fig. II-5   Fig. II-6

Finally, it is of interest that the apical iridium-

phosphorus bond Ir-P(1) is significantly shorter than the

equatorial bond Ir-P(2) by 0.043Å. This probably reflects the

absence of a ligand trans to P(1). As this appears to be the

first example of a five-coordinate iridium complex containing

phosphine ligands in both apical and basal positions, it is

difficult to draw exact comparisons, particularly as Ir-P bond

lengths in the literature[23,48,49] show considerable variation

with the number and type of ligands present and their disposi-

tion; the values are, however, in agreement with other Ir-P

bond lengths[23,48].

D. Properties

1. General Properties

The aryltetrazene complexes, 4a-f, are deep-red, crystal-line solids. They are quite stable over prolonged periods in air and appear to be stable to moderate heating, as demonstrated by their decomposition temperatures listed in Table II-2.

The complexes are soluble in ethanol, methanol, acetone, acetonitrile, nitromethane, chloroform and dichloromethane, and insoluble in benzene, ether, n-hexane, n-pentane and water. They appear to be unstable in chlorinated solvents, the product obtained on recrystallisation from dichloromethane giving high and irrational analysis for chlorine. There is also some instability in ethanol solution, as indicated by a decrease in the molar absorptivity, ϵ 500nm with time.

The conductance of the aryltetrazene complexes in nitro-methane solution is typical of 1:1 electrolyte behaviour[44]; the relevant data for the para-fluoro complex, 4b, and other comparable 1:1 electrolytes is given in Table II-3.

Magnetic susceptibility measurements showed the aryl-tetrazene complexes to be diamagnetic, as expected. Along with the observation that the (i.r.) carbonyl stretching modes of the complexes, 4a-f, lie between 2035 and 2064 cm^{-1} (Table II-5) they can thus be formulated as complexes of iridium(III).

Table II-3

Molar
Conductances in Nitromethane Solution at 25°C

Electrolyte	Molar Concentration	Molar Conductance, Λ_M ohm^{-1}mole^{-1}cm^2
$[Ir(CO)\{N_4(C_6H_4F)_2\}(PPh_3)_2]BF_4$ (4b)	3.7×10^{-4}	105
	1.5×10^{-4}	117
$[Ir(CO)Cl(NO)(PPh_3)_2]BF_4$	1.7×10^{-4}	100
	6.6×10^{-4}	116
$C_6H_5N_2BF_4$	4.5×10^{-4}	115
$NaBPh_4$	3.7×10^{-4}	90

On pyrolysis of the complex $\underset{\sim}{4}$b at 540°C under high
vacuum, and subsequent gas chromatographic analysis of the non-
condensible gases, it was found that for each mole of complex
one mole of carbon monoxide and one mole of dinitrogen were
evolved. This result mitigated against the initial suspicion
of a bis-arylazo complex, which would be expected to evolve
two moles of dinitrogen on pyrolysis.

2. Infrared Spectroscopy

The main absorptions observed, as exemplified by the
para-fluoro complex, $\underset{\sim}{4}$b, are recorded in Table II-4 and illus-
trated in Diagram II-2. For comparison, Table II-4 also
includes infrared data on the reactants leading to the aryl-
tetrazene complex $\underset{\sim}{4}$b, i.e., Vaska's complex $\underset{\sim}{1}$ and para-
fluorophenyldiazonium tetrafluoroborate. No bands assignable
to N=N·stretching were detected. Isotopic (N^{15}) substitution
at the terminal nitrogen of the aryldiazonium cation failed
to show a frequency shift for any of the vibrations of complex
$\underset{\sim}{4}$b. Raman spectra are unavailable owing to decomposition of
the aryltetrazene complexes in He-Ne laser radiation.

The most significant variation in the infrared spectra
of the complexes $\underset{\sim}{4}$a-f is in the position of the carbonyl
stretching mode. The frequencies of the various carbonyl
stretching vibrations and the values of the Hammett σ-constants
for the para-substituents on the $N_4(C_6H_4R)_2$ moieties of the
complexes $\underset{\sim}{4}$a-f are given in Table II-5.

Table II-4

Comparison of Infrared Spectra of $[Ir(CO)Cl(PPh_3)_2](1)$, $[Ir(CO)\{N_4(C_6H_4F)_2\}(PPh_3)_2]BF_4(4b)$ and $p\text{-}FC_6H_4N_2BF_4$.

Position of Absorption (cm^{-1})^a			Assignment[38,39]
Compound (1)	$p\text{-}FC_6H_4N_2BF_4$	Compound (4b)	
3060(w-m)	3110(s) 3060(m) 3080(m)	3060(w-m)	Aromatic C-H stretching
	2297(s)		N≡$\overset{\oplus}{N}$ stretching
1965(s)		2057(s)	C≡O stretching
1435(s) 1480(s) 1570(w) 1590(w)	1435(m) 1485(s) 1580(s)	1435(s) 1480(m) 1500(s) 1595(m)	Aromatic C=C stretching
	1255(s)	1220(s)	C-F stretching
1100(s)			PPh$_3$ deformation
	1010-1170(s,br)	1030-1100(s,br)	BF$_4^-$ stretching
	850(s)	840(m-s)	Aromatic C-H bending (two adjacent hydrogen atoms)
695(s) 750(s)		695(s) 745(s)	Aromatic C-H bending (five adjacent hydrogen atoms)
500(s) 510(s) 520(s)	525(s) 535(s)	515(s) 535(m-s) 560(m)	Aromatic absorptions and BF$_4$ deformation
315			Ir-Cl stretching

a   w = weak; m = medium; s = strong; br = broad
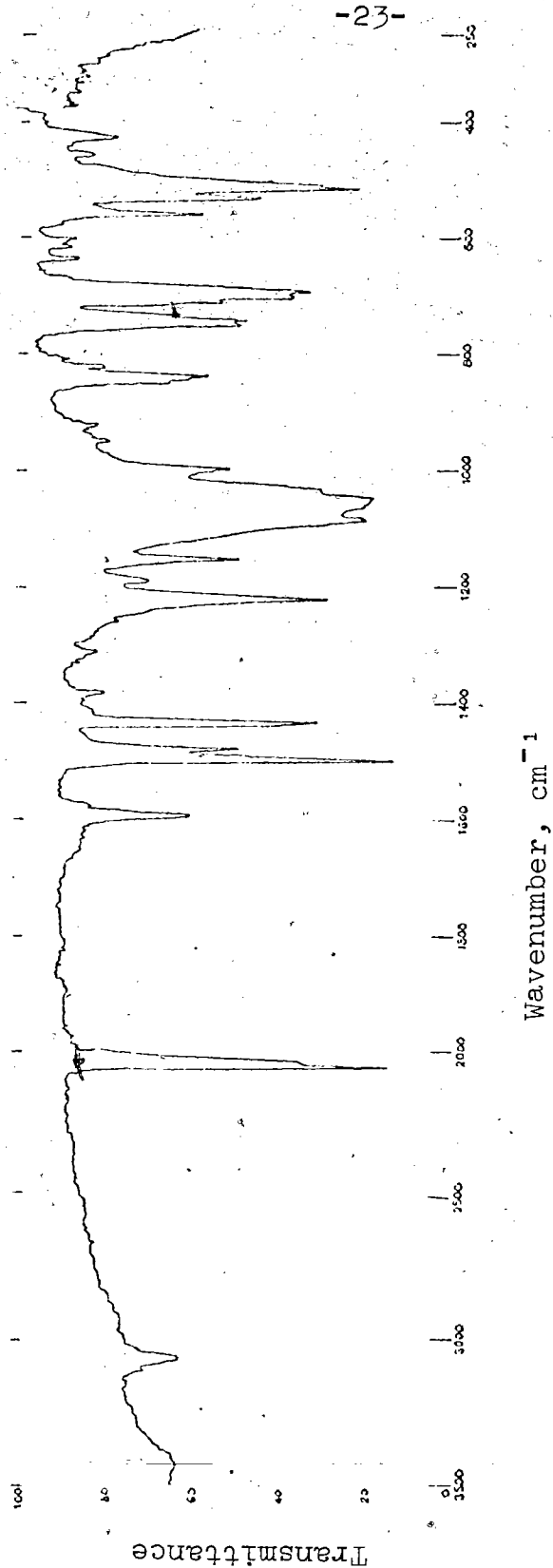
Diagram II-2. Infrared spectrum of $[Ir(CO)(PPh_3)_2\{N_4(C_6H_4\underline{p}\text{-}F)_2\}]BF_4$, 4b

Table II-5

Relationship Between the Carbonyl Stretching
Frequency (ν_{CO}) of the Aryltetrazene Complexes,
4a-f, and the Hammett Substituent Constants, σ_p,
of the para-Substituents Associated with
the $N_4(C_6H_4R)_2$ Moiety.

Compound (R)	ν_{CO} ($\pm$ 1 cm^{-1})	σ_p
4f (OCH$_3$)	2035	-0.27
4a (H)	2037	0
4b (F)	2057	0.06
4c (Cl)	2057	0.23
4d (Br)	2059	0.23
4e (CF$_3$)	2064	0.54

It has been suggested[40,41] that the CO stretching
vibration may be used as a criterion for any change in electron
density at the metal in an oxidative addition adduct as
compared to the parent compound (complex 4a in this instance).
Thus, an electron-withdrawing substituent would be expected to
decrease the electron density at the metal resulting in decrease
in the amount of back-donation from the metal to the CO ligand;
this would be reflected by a raising of the energy of the ν_{CO}
vibration, and vice-versa for an electron-releasing substituent.
A straight-line relationship between ν_{CO} and the Hammett substi-
tuent parameter, σ_p, has been claimed for a series of para-
substituted iridium benzenethiol complexes,
[$IrHCl(SC_6H_4R)(PPh_3)_2$] (R = H; p-NO$_2$, Br, Cl, F, CH$_3$, OCH$_3$)[40].
Although there is a definite trend for the carbonyl stretching
frequencies in these complexes to increase with the electron-
accepting power of the para-substituent, and vice-versa, the
claim for a straight-line relationship appears to be somewhat
tenuous in that, apart from the extreme ends (p-NO$_2$ and p-OCH$_3$)
of the series, the ν_{CO} (cm^{-1}) values are virtually invariant.
In the aryltetrazene complexes, 4a-f, although there is no
straight-line relationship, there is also an obvious trend for
the ν_{CO} vibration (which should parallel the force constant)
to increase as the electron-withdrawing ability of the para-
substituent associated with the N$_4$(C$_6$H$_4$R)$_2$ moiety increases
(c.f. Table II-5). This indicates that the electron-withdrawing

effect of the para-substituent is relayed to the iridium, resulting in a decreased transfer of electrons from the iridium d-orbitals to the π-antibonding orbitals of the CO ligand. The non-linear relationship between the CO stretching frequency of the adducts 4a-f and the electron affinities of the variously substituted aryltetrazene ligands may be due to an electrostatic contribution that is absent for the molecular complexes studied by other workers[40,41].

3. Nuclear Magnetic Resonance Spectroscopy

The presence of both p-F and BF_4^- in complex 4b, already indicated from infrared spectroscopy, conductance and elemental analysis, was confirmed by ^{19}F nmr spectroscopy in $CDCl_3$ solution (at 56.4 MHz) using CAT[a]. A weak signal at +6230 Hz and a strong signal at +8778 Hz, downfield relative to a CCl_3F internal standard, were assigned to p-F and BF_4^-, respectively. The shifts are comparable with those of +6135 Hz (p-F) and +8585 Hz (BF_4^-) reported for the arylazo complex $[PtCl(N_2C_6H_4p-F)(PEt_3)_2]$[4,5].

The proton nmr spectrum of complex 4b in $CDCl_3$ solution showed broad multiplet peaks centred at τ 2.9 and τ 3.8 relative to TMS as internal standard, with integrated intensities equivalent to 40 protons and ≴ protons, respectively. Both the triphenylphosphine and benzene entities, which exhibit proton nmr signals at ca. τ 2.8 in the free state, undoubtedly contribute to the downfield absorption. In the grouping $FC_6H_4N-N=$

a. Computer averaged transients
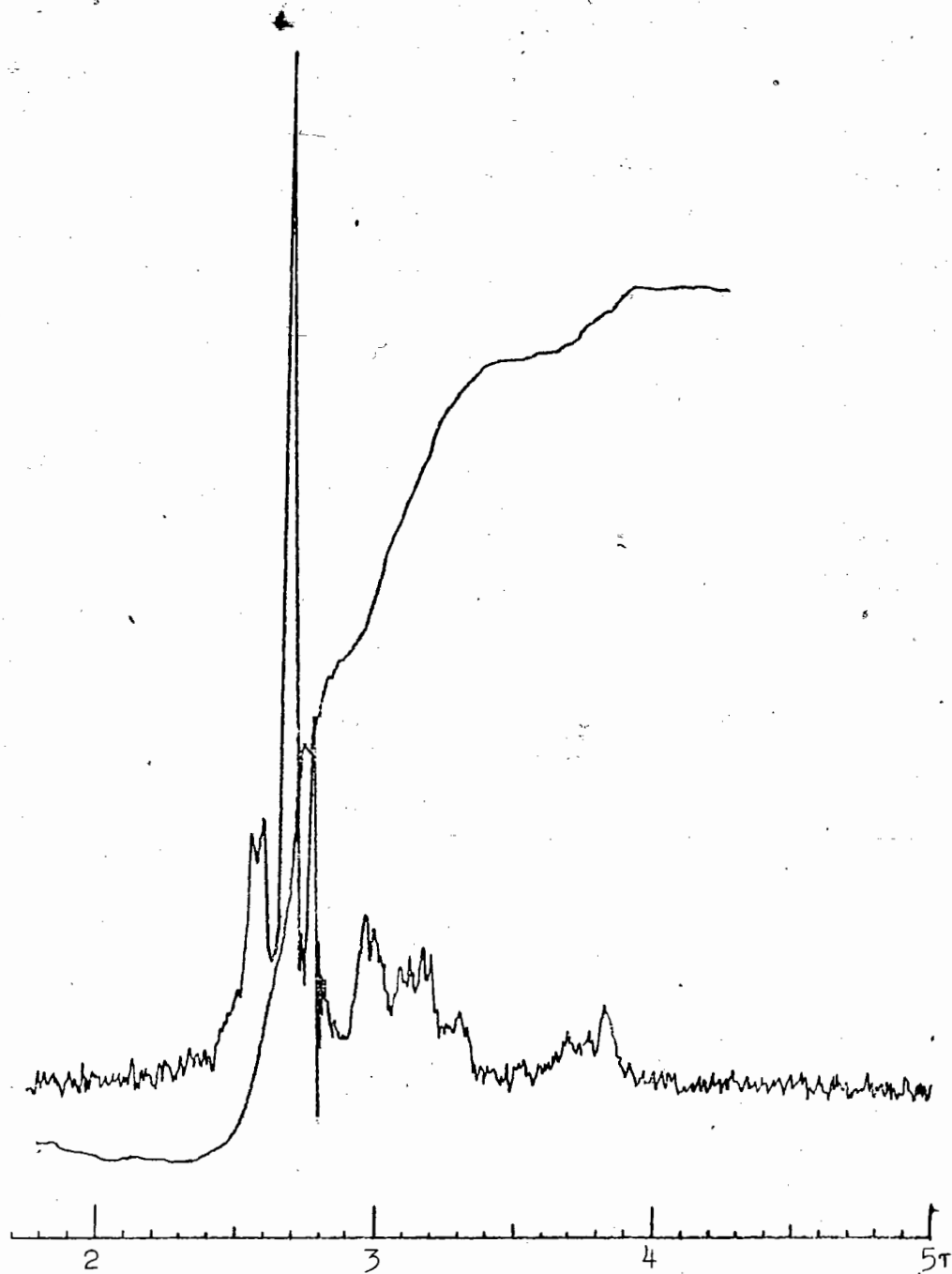
Diagram II-3. Proton n.m.r. spectrum of

$[Ir(CO)(PPh_3)_2\{N_4(C_6H_4\underline{p}-F)_2\}]BF_4$, $\underset{\sim}{4}b$

Table II-6

^{1}H and ^{19}F N.M.R. Spectroscopy of
$[Ir(CO)\{N_4(C_6H_4p\text{-}F)_2\}(PPh_3)_2]BF_4 \cdot C_6H_6$

	Chemical Shift		Relative Integrated Intensity	Assignment
	τ (Relative to TMS)	cps (Relative to CCl_3F)		
(a)H'nmr	2.9		10	See pp26,29
	3.8		1	
(b)^{19}Fnmr		+6230		p-F
		+8778		BF_4^-

(see Fig. II-7), H_A and $H_{A'}$ are chemically equivalent and will
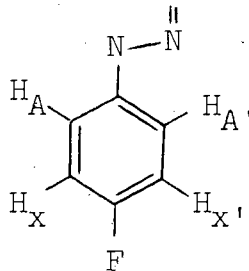
Fig. II-7

exhibit a different chemical shift from H_X and $H_{X'}$, also chemically equivalent. This will result in two sets of multiplets, each integrating for four protons (there being two such $FC_6H_4N-N=$ groupings). It seems likely, then, that the multiplet-centred at τ 2.9 consists of the 40 protons from the two PPh_3 ligands, the downfield four-proton multiplet of the two $FC_6H_4N-N=$ groupings and the one C_6H_6 of crystallisation, whereas the multiplet centred at τ 3.8 is due to the upfield four-proton signal of the two $FC_6H_4N-N=$ groupings. The complex splitting patterns, further complicated by overlapping of the signals, has not been resolved. An illustration of the proton nmr spectrum is provided in Diagram II-3 and the data from both the ^1H and ^{19}F spectra are summarised in Table II-6.

4. Electronic Spectroscopy

Electronic spectral data for the aryltetrazene complexes 4a-f are listed in Table II-7. The spectra are characterised

Table II-7

Electronic Spectral Data for the Aryltetrazene
Complexes $[Ir(CO)\{N_4(C_6H_4R)_2\}(PPh_3)_2]BF_4$ (4a-f)

Compound (R)	Wavelength (λ, nm) and Molar Absortivity (ϵ, $m^{-1}cm^{-1}$) Maxima[a]					
	λ_1	ϵ_1	λ_2	ϵ_2	λ_3	ϵ_3
4f (p-OCH$_3$)	360	4515	420-490	4736	500	4462
4a (H)	390	5544	440	5544	500	3960
4b (p-F)	400	6247	440	6085	500	3948
4c (p-Cl)	406	8116	440	7558	500	5224
4d (p-Br)	410	9417	440	9116	500	5819
4e (p-CF$_3$)	385	8656	440	7243	500	5182
1 [Ir(CO)Cl(PPh$_3$)$_2$]	339	3155	386	3800	436	738

a In absolute ethanol at 25°C.
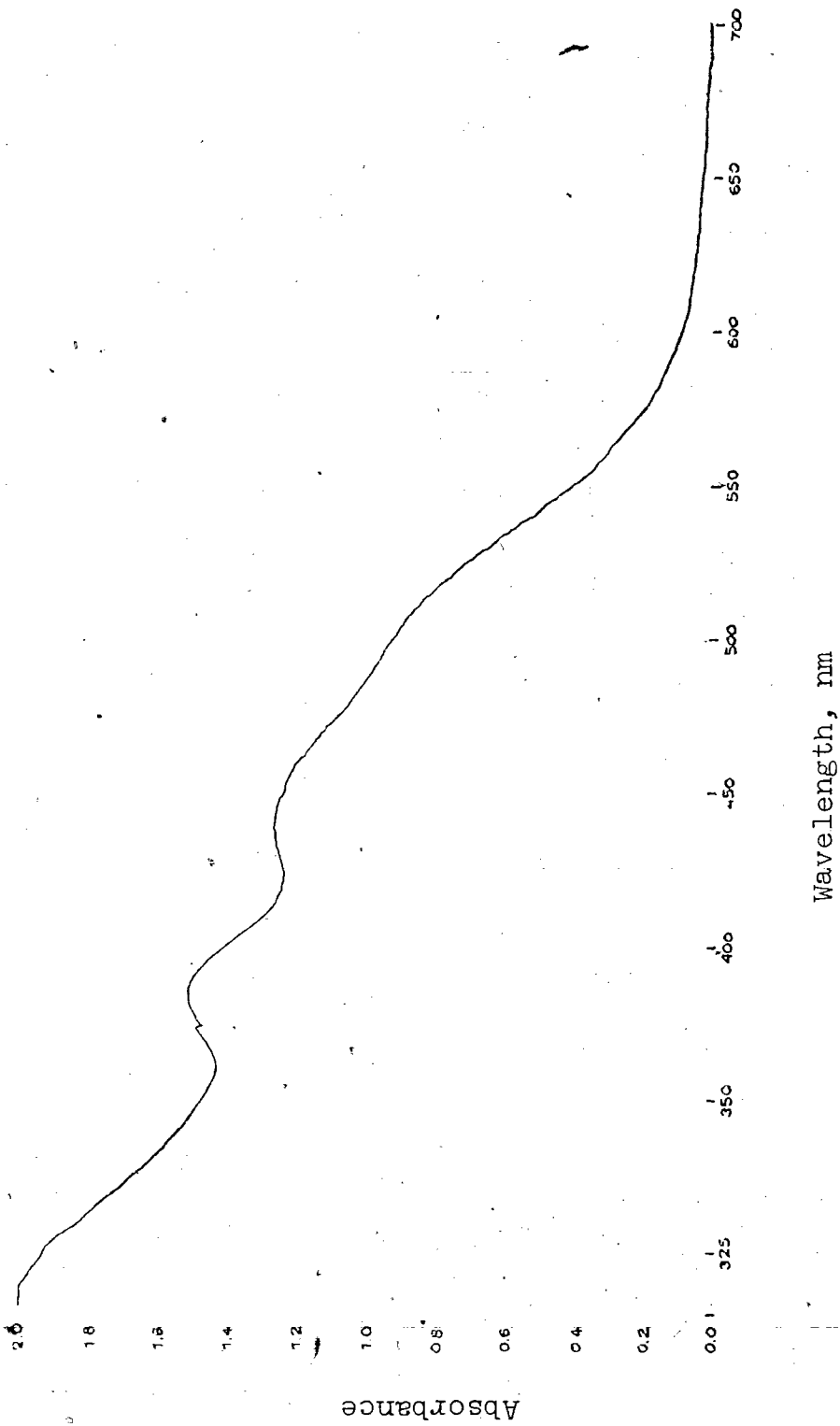
Diagram II-4. Visible spectrum of $[Ir(CO)(PPh_3)_2\{N_4(C_6H_4\underline{p}-CF_3)_2\}]BF_4$, $\underline{4e}$
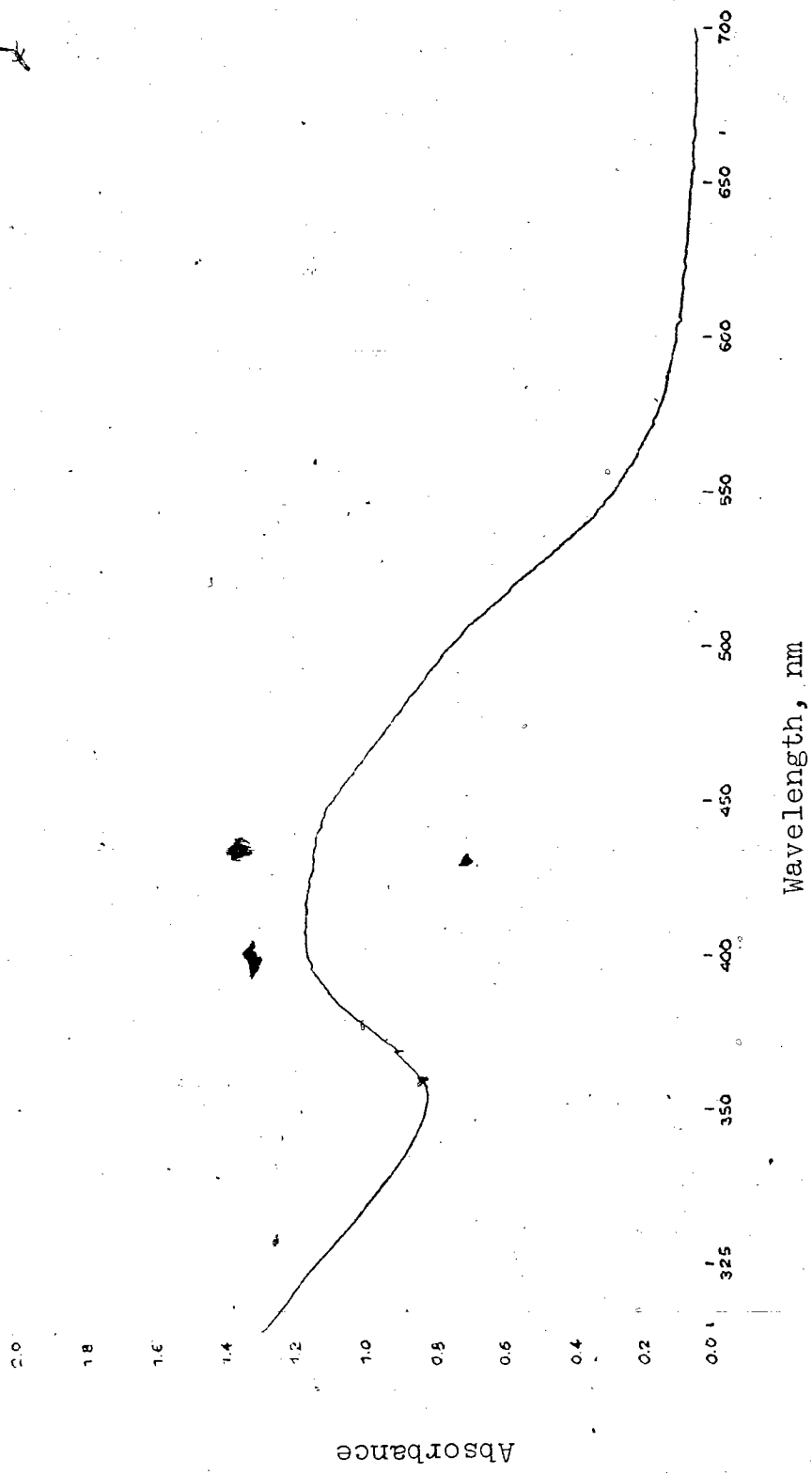
Diagram II-5. Visible spectrum of $[Ir(CO)(PPh_3)_2\{N_4(C_6H_4p\text{-}\underline{F})_2\}]BF_4$, 4b

by three absorption bands in the region between 350 nm and 600 nm. Generally, these bands overlap to such an extent that they appear essentially as a single broad absorption from which the maxima can only be approximately discerned. The most clearly resolved spectrum is afforded by the p-CF$_3$ complex 4e, and the least clearly by the p-F complex 4b; these two spectra are shown in Diagrams II-4 and II-5.

A comparison of the spectra of the aryltetrazene complexes with those of Vaska's complex, 1, the aryldiazonium tetrafluoroborate salt and the aryldiimide complexes, 5, revealed that the absorption in the 500 nm region is exclusive to the aryltetrazene complexes. That this absorption, with a molar absorptivity varying from approximately 4000 to 6000, might be due to a transition ($\pi^* \leftarrow \pi$; $\pi^* \leftarrow n$) associated with the tetrazene ligand was negated by the observation that no energy shift resulted on changing the solvent from ethanol to dichloromethane, or on changing the R substituent in the complexes 4a-f. In fact, all three bands remained insensitive to the solvent change, indicating that the absorptions are associated mainly with the metal rather than with the ligand.

Vaska's complex, 1, in benzene solution exhibits three well defined bands at 339 nm (ϵ = 3155), 386 nm (ϵ = 3800) and 436 nm (ϵ = 738) which are assigned to d-d transitions[42] and are consistent with model planar d^8 systems described in the literature[43]. No direct comparison can sensibly be made

between the spectra of the square-planar Ir(d^8) system, $\underset{\sim}{1}$, and the irregular five-coordinate square-pyramidal Ir(d^8) aryl-tetrazene cation, $\underset{\sim}{4}$. That the three maxima discernible in the broad envelope (ca. 350-600 nm) observed in the spectra of the aryltetrazene complexes may be largely due to three such d-d transitions is feasible, but, on the other hand, may simply be coincidental, many other transitions (such as charge-transfer, $\pi^*\leftarrow\pi$, further d-d transitions) probably also contributing. On changing the substituent R in the complexes $\underset{\sim}{4}$a-f, the high-energy band in the spectrum shifts to lower energy and the molar absorptivity increases as the electron-acceptor power of the R substituent increases; although not conclusive, this is consistent with charge-transfer from iridium to the aryltetrazene ligand.

The fact that the complexes $\underset{\sim}{4}$a-f absorb in a region (around 500 nm) in which neither the reagents involved in their syntheses nor the other isolable complex, $\underset{\sim}{5}$, absorb, allowed a spectrophotometric assay of the maximum amount of aryltetrazene complex actually formed. From the molar absorptivity of the pure complexes $\underset{\sim}{4}$a-f at 500 nm and the absorptions of the reaction solutions, also at 500 nm, the maximum amount of aryltetrazene complex formed was calculated. The yields thus found are recorded in Table II-2, along with the yields actually isolated. The most obvious inference from these "spectrophotometric yields" is that the formation of the aryl-

tetrazene complex increases with increasing electron-acceptor power of the R substituent. The significance of this is discussed in Chapter VII B.

By following the course of the reactions spectrophotometrically, it was observed that reaction, with respect to aryltetrazene complex formation, was complete after 45-60 minutes. Reaction times greater than 90 minutes resulted in a decrease in tetrazene formation.

E. Discussion

An intriguing point of interest regarding the iridium aryltetrazene complexes, 4a-f, is their mode of formation from aryldiazonium cations. As already pointed out, all other known metal tetrazene complexes have been prepared from organic azides. Here, probable mechanistic routes can be readily proposed. For example, the formation of both $[Fe(N_4Me_2)(CO)_3]$ (from $Fe_2(CO)_9$ and CH_3N_3) and $[Ni\{N_4(C_6F_5)_2\}(1,5-C_8H_{12})_2]$ from $Ni(1,5-C_8H_{12})_2$ and $C_6F_5N_3$ has been considered to involve the catalytic generation of a nitrene complex (M-NR) which then reacts with a further molecule of the azide yielding the complexed N_4R_2 ligand[30,33]. An alternative approach involves the formation of a cationic dinitrogen complex.[33] These two schemes are outlined in Figure II-8.

$$M + R\text{-}\overline{N}\text{-}N{\equiv}N^{+}$$
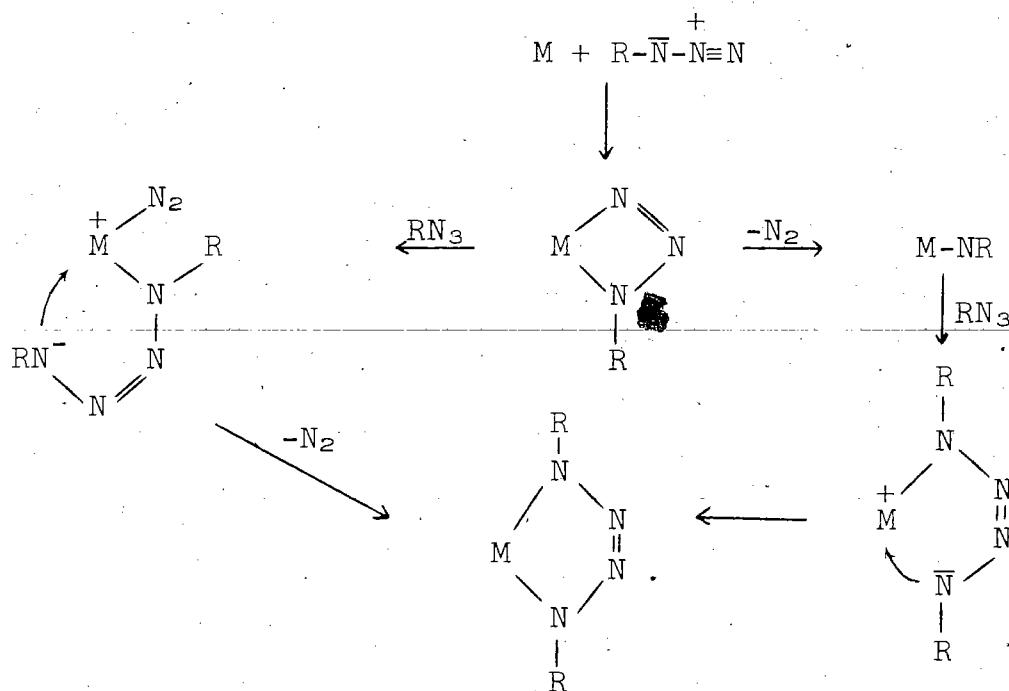
Fig. II-8

A reaction path leading to aryltetrazene complexes via ArN_2^{+} is not so readily visualized. Formally, the tetrazene moiety can be viewed as resulting from the coordination of two aryldiazonium groups, to the iridium through their bound nitrogen atoms, with linking together of their free nitrogen atoms. No examples have been found in the literature where an aryldiazonium cation bonds to a second entity via its bound nitrogen atom, and it is also unlikely that this occurs in the formation of the iridium aryltetrazene complexes. A possible route, however, involves the reduction of ArN_2^{+} to an aryl-

diazene intermediate (ArN=NH) which then reacts with a further
molecule of ArN_2^+ leading to a bis-aryl N_4 species which, in
turn, coordinates to the metal. Evidence for this mechanistic
path is presented in Chapter VII.

The possible linking of two arylazo ligands to form a
complexed tetrazene moiety may, however, have some significance
with respect to the nitrogen fixation process[51]. This would
require invoking a new model in which two dinitrogen moieties
bound on similar adjacent sites are activated by simultaneous
binding to a third, different metal through the 1 positions,
and linked together by the 2 positions, as illustrated in
Fig. II-9. The lowering of N-N bond strength inherent in such
a model would be considerable.

$$M\diagup N\!\!\equiv\!\!N \qquad N\!\!\equiv\!\!N\diagdown M \quad\longrightarrow\quad M\!-\!N\!\!\diagup\!\!\overset{N=N}{}\!\!\diagdown\!\!N\!-\!M$$
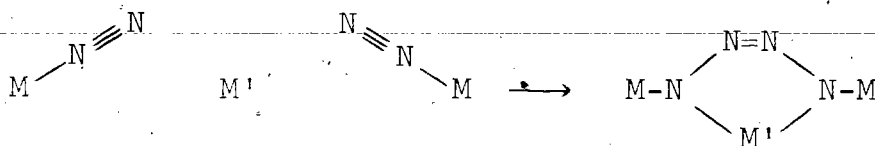
Fig. II-9

X-ray crystallographic data (Chapter II-C) for the iridium
aryltetrazene complex, 4b, show that the central bond length
corresponds to an N=N double bond and the outer bond lengths
approximate to single bonds, whereas these were triple bonds in
the original diazonium salt. Little attention seems to have
been given to the possibility of "polymerization" of the dini-
trogen molecule occurring in nitrogen fixation, although
Shustorovitch[52] has entertained this possibility on theoretical
grounds.

CHAPTER III

Cationic ortho-Metalated Aryldiimide Complexes

A. Introduction

While synthesising the aryltetrazene series, 4, the

reaction between Vaska's complex, 1, and the para-bromophenyl-

diazonium salt, p-BrC$_6$H$_4$N$_2^+$.BF$_4^-$, afforded a second entirely

unexpected, yellow, crystalline product. By suitable adjust-

ment of (a) the ratio of the two solvents employed (benzene

and ethanol) and (b) the isolation technique, a yellow compound

was also obtained from the para-fluorophenyldiazonium salt,

p-FC$_6$H$_4$N$_2^+$BF$_4^-$, in a crystalline form suitable for X-ray

diffraction studies. This diamagnetic, air-stable complex has

been characterised by various techniques, including an X-ray

structure determination[54,55], as an ortho-metalated aryldiimide

complex. Two series of these complexes, 5a-q and 5j,r-u

(Fig. III-1 and Fig. III-2, respectively) have been synthesised

and characterised.

The complexes 5a-q are isomers of the anticipated arylazo

adducts [Ir(CO)Cl(N$_2$Ar)(PPh$_3$)$_2$]$^+$BF$_4^-$; they are analytically

indistinguishable.

Series 5j,r-u resulted from experiments to ascertain the

effect on the course of the reaction between Vaska's complex,

1, and ArN$_2^+$ of varying the phosphine and the anionic ligands

$$\left[\begin{array}{c} N \!\!=\!\! NH \\ Ir(CO)Cl(PPh_3)_2 \\ R \end{array} \right]^{+} \quad BF_4^{-}$$

Fig. III-1

5a, R=H.
~b, p-F
 c, p-Cl
 d, p-CH₃
 e, p-Br
 f, p-NO₂

g, R=pCF₃
h, o-F
i, o-Cl
j, o-Br
k, o-NO₂
l, m-CH₃

m, R=m-OCH₃
n, m-Br
o, m-Cl
p, m-NO₂
q, m-F

$$\left[\begin{array}{c} N \!\!=\!\! NH \\ Br Ir(CO)A(PPh_3)_2 \\ \end{array} \right]^{+} \quad Y^{-}$$
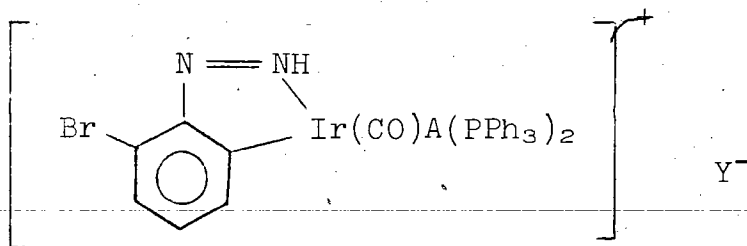
Fig. III-2

5j, A=Cl;   Y=BF₄
~r, A=F;   Y=BF₄
 s, A=I;   Y=BF₄
 t, A=Br;   Y=BF₄
 u, A=OClO₃; Y= ClO₄

(c.f. Chapter IIIB, p43, and Chapter VII).

The members of the series were synthesised from the ortho-bromophenyldiazonium salt, $o-BrC_6H_4N_2^+BF_4^-$, as it had previously been found to afford the most consistently high yields in the syntheses of 5a-q.

B. Synthesis

The aryldiimide complexes, 5a-u, were prepared by reacting Vaska's complex, 1, or the requisite analogue $[Ir(CO)A(PPh_3)_2]$ (A = F, Br, I, $OClO_3$), with the requisite aryldiazonium tetrafluoroborate, ArN_2BF_4, in benzene-ethanol. The mole ratio of ArN_2BF_4 to the iridium complex was held at 1:1. The benzene:ethanol ratio was fixed at 3:1 (by volume), whereas in the aryltetrazene syntheses it was held at 10:1. In certain instances, both the aryltetrazene and the aryldiimide complexes were isolated irrespective of whether the benzene:ethanol ratio was 10:1 or 3:1; however, the 3:1 ratio was found to favour isolation of the aryldiimide complexes. As previously mentioned (Chapter II B), with the 10:1 ratio the aryltetrazene complex generally crystallised out on cooling of the reaction solution, whereas with the 3:1 ratio no crystallisation occurred. In the latter case, the solvent was removed by a freeze-drying procedure and the resulting solid was stirred with benzene. Generally, the benzene-insoluble fraction

Table III-1

Elemental Analyses and Yields for
the Aryldiimide Complexes,
$[\text{IrA(CO)(HNNC}_6\text{H}_3\text{R)(PPh}_3)_2]\text{Y,}^{(a)}$ 5a-u

Compound			Percentage Composition						Percentage Yield
			Found			Calculated			
No.	R	A	C	H	N	C	H	N	
5a	H	Cl	55.39	3.67	2.72	56.04	3.93	2.67[b]	2
5b	p-F	Cl	52.65	3.88	2.85	52.70	3.85	2.67[c]	13
5c	p-Cl	Cl	52.84	3.57	2.59	52.83	3.57	2.68[d]	8
5d	p-CH$_3$	Cl	53.40	3.73	2.81	53.58	3.78	2.84	4
5e	p-Br	Cl	48.98	3.25	2.76	49.14	3.26	2.67[e]	22
5f	p-NO$_2$	Cl	49.64	3.45	5.35	50.78	3.37	4.13	3
5g	p-CF$_3$	Cl	51.54	3.77	2.37	51.40	3.67	2.55[c]	8
5h	o-F	Cl	52.12	3.46	2.79	52.16	3.46	2.83	13
5i	o-Cl	Cl	52.08	3.93	2.69	51.89	3.79	2.63[c]	13
5j	o-Br	Cl	50.07	3.80	2.49	49.80	3.64	2.53[c]	17
5k	o-NO$_2$	Cl	50.58	3.57	3.91	50.78	3.37	4.13	13
5l	m-CH$_3$	Cl	53.48	3.83	3.10	53.58	3.78	2.84	22
5m	m-OCH$_3$	Cl	53.66	4.09	2.68	53.25	4.09	2.64[c]	8
5n	m-Br	Cl	49.28	3.30	2.61	49.14	3.26	2.67	8
5o	m-Cl	Cl	50.92	3.56	2.68	51.31	3.41	2.78	13
5p	m-NO$_2$	Cl	50.17	3.37	3.96	50.78	3.37	4.13	14
5q	m-F	Cl	50.90	3.57	2.65	52.16	3.46	2.83	14
5r	o-Br	F	50.46	3.73	2.70	50.56	3.69	2.55[c][f]	29
5s	o-Br	I	45.66	3.05	2.55	45.19	3.00	2.45[g]	14
5t	o-Br	Br	48.53	3.28	2.50	48.70	3.29	2.47[d]	16
5j	o-Br	Cl	50.07	3.80	2.49	49.80	3.64	2.53[c]	17
5u	o-Br	OClO$_3$	46.68	3.25	2.41	46.59	3.40	2.36[c][h]	43

(a) $5a-t$, $Y = BF_4$; $5u$, $Y = ClO_4$

(b) Formulated with 1 mole C_6H_6 per mole of complex.

(c) Formulated with 1 mole $(CH_3)_2CO$ per mole of complex.

(d) Formulated with 0.5 mole C_6H_6 per mole of complex.

(e) Chlorine (Cl) analysis: Found 3.23%; Calculated 3.37%

   Bromine (Br) analysis: Found 7.56%; Calculated 7.60%

(f) Fluorine (F) analysis: Found 8.54%; Calculated 8.69%

(g) Iodine (I) analysis: Found 11.08%; Calculated 11.10%

(h) Chlorine (Cl) analysis: Found 6.08%; Calculated 5.98%

   Bromine (Br) analysis: Found 7.19%; Calculated 6.75%

was carefully recrystallised from acetone-ether resulting,
first, in precipitation of the yellow, crystalline aryl-diimide
complex, followed by precipitation of the red, crystalline
aryltetrazene complex. Detailed procedures are given in
ChapterVII,but it should be noted here that, depending on the
ring substitution of the aryldiazonium cation, (a) the aryl-
diimide complex was sometimes obtained from the benzene-
soluble fraction, and (b) isolation of the aryltetrazene com-
plex was not always achieved; in fact, it was achieved only
for para-substituted aryldiazonium cations, as discussed in
Chapter II B.

Table III-1 lists the aryldiimide complexes isolated and
characterised, along with their elemental analyses and yields.

Attempts to synthesise aryldiimide complexes of the more
nucleophilic analogues of Vaska's complex, 1, namely,
$[Ir(CO)Cl(PMePh_2)_2]$ and $[Ir(CO)Cl(PMe_2Ph)_2]$ proved unsuccessful;
this was also the case with regard to the aryltetrazene com-
plexes. The mechanistic implication of this is discussed in
Chapter VII.

C. Structure

A single crystal X-ray structural analysis of the complex
5b, chloro-carbonylbis(triphenylphosphine) 4-fluoro, 6-iridio-
phenyldiimide tetrafluoroborate, revealed the structure to
consist of an array of discrete six-coordinate iridium complex
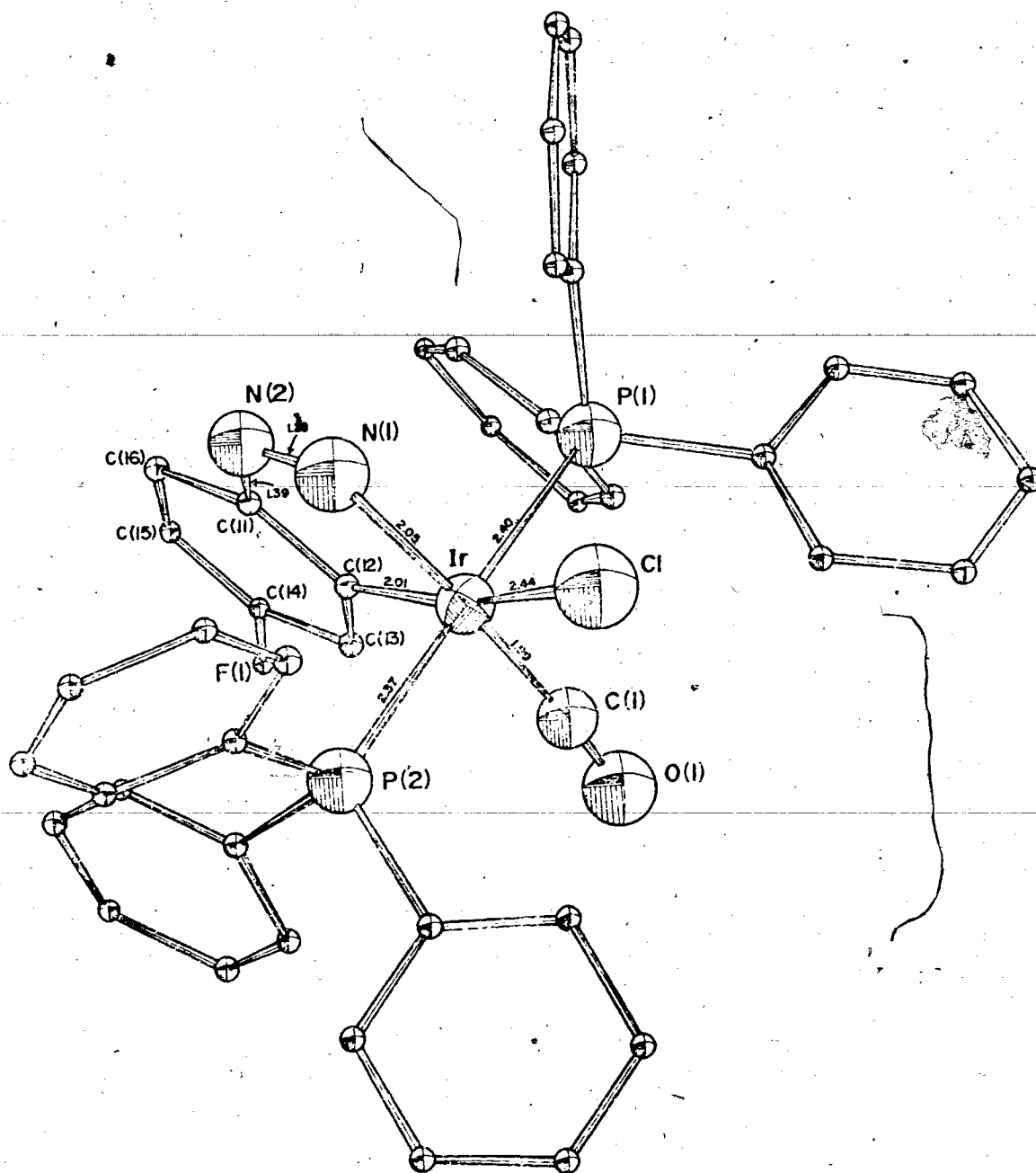
Diagram III-1.   Molecular configuration of

$[\overline{Ir(CO)Cl(PPh_3)_2(HNNC_6H_3\underline{p}\text{-}F)}]^+$, 5b
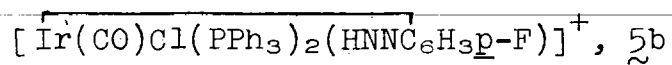
cations and tetrafluoroborate anions together with acetone
molecules of crystallisation (one acetone molecule per iridium
atom)[54,55]. The molecular configuration of the cation is
shown in Diagram III-1.

The environment of the iridium is that of a distorted
octahedron, the distortion being imposed by the presence of
the five-membered ring. Leaving aside the apical triphenyl-
phosphine groups, the remaining 'equatorial' atoms of the
complex cation are very nearly coplanar. Noticeably, the
phosphine groups are <u>trans</u> and the Ir-P lengths are almost
identical with the longer of the two distinctly different Ir-P
bond lengths in the pentacoordinate tetrazene complex, where
the phosphines are <u>cis</u> (Chapter II C and Diagram II-1), and
agree closely with the Ir-P lengths of the <u>trans</u>-phosphine
groups in the similar complex $[IrCl_2(p-CH_3OC_6H_3N_2H)(PPh_3)_2] \cdot CHCl_3$
described by Bellon <u>et al</u>.[53, 182]

The principal feature of the complex cation is the
internal metalation of the aryldiimide ligand at atom C(12) to
give a five-membered heterocyclic ring. This process, ortho-
metalation, has been recognised as an important substitution
reaction of aromatic compounds possessing a nitrogen[56-74,174] or
phosphorus[75-87] donor atom and numerous examples have appeared
since the subject was reviewed[88]. Although the phenomenon is
reasonably well established on chemical and spectroscopic
(i.r. and n.m.r.) evidence, only a few crystal structure deter-

minations have been reported[63,69,77,89], and none in detail.

The five-membered ring in 5b is closely similar in dimensions
to the corresponding ring in acetatobis-[(2-phenylazo)phenyl]
rhodium, as reported by Craik et al.[63] The Ir-C(12) and
Ir-N(1) bond lengths in the chelate ring of 5b are not signi-
ficantly different. As Craik et al.[63] do not report errors,
it cannot be decided whether the corresponding distances are
different in the rhodium compound; however, the closely
related ortho-metalated phenyl ring in a manganese-benzilidene-
aniline complex[69] is bound to manganese with identical Mn-C
and Mn-N distances. A comparison of the molecular geometry of
the recently determined complex [IrCl$_2$(p-CH$_3$OC$_6$H$_3$N$_2$H)(PPh$_3$)$_2$]·CHCl$_3$
[53,182] with that of 5b shows that there is strict similarity between
corresponding interactions in both structures. The N(1)-N(2)
bond length of 1.28Å in 5b indicates this to be a conventional
double bond, again similar to the related compounds just
mentioned.[53,63,69]

The presence of an N-H bond in 5b has been established by
i.r. (Chapter III-D2) and n.m.r. (Chapter III-D3) spectroscopy,
and by deprotonation with base (Chapter IV). Although the
X-ray diffraction data do not unambiguously confirm the presence
of the proton on N(1), they are more consistent with the site
being N(1) rather than N(2); this is chemically sensible in so
far as the hydrogen atom then has the position occupied by the
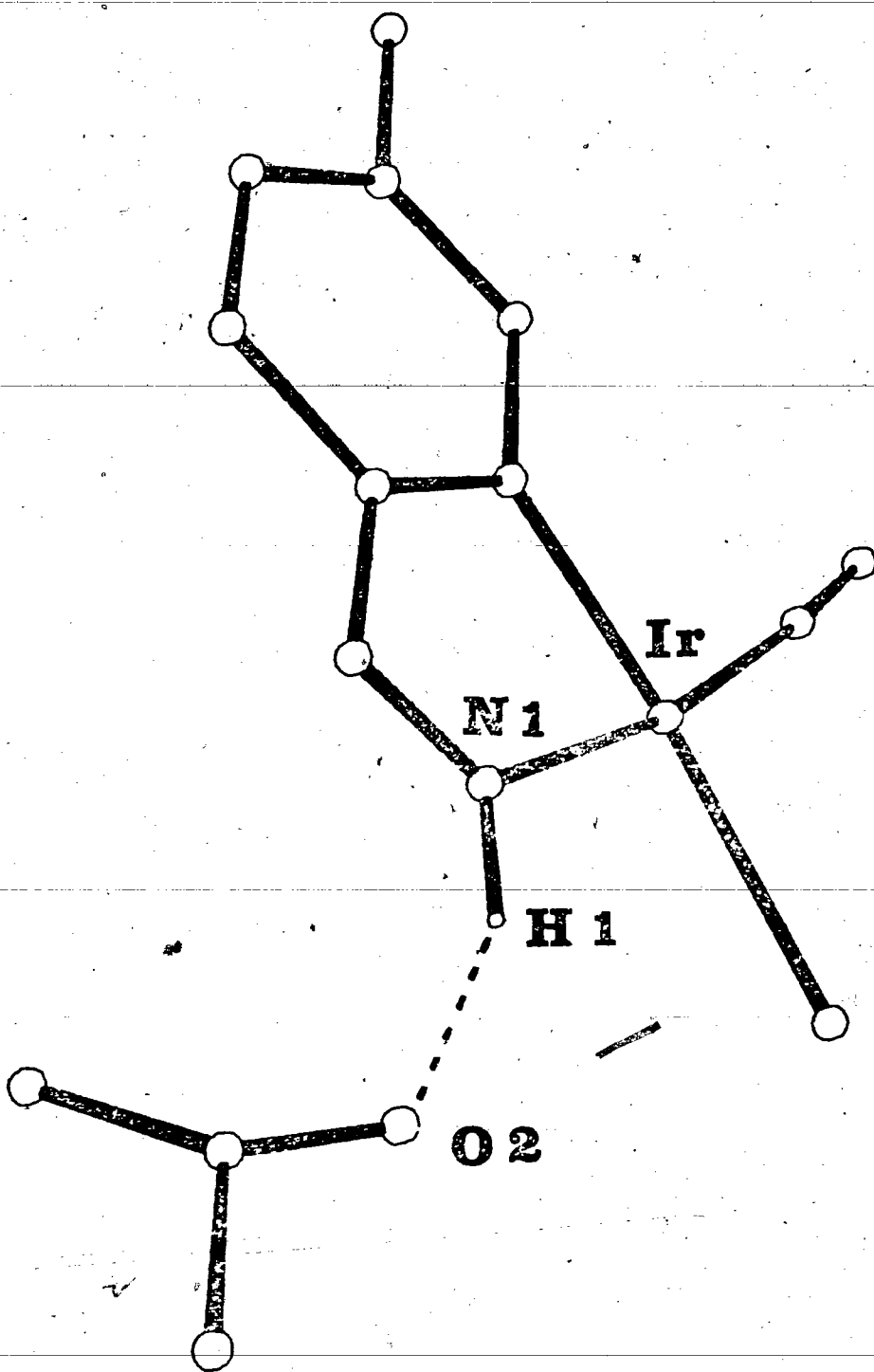
Diagram III-2. Intermolecular hydrogen bonding between acetone and H_1 in

$$[Ir(CO)Cl(PPh_3)_2(HNNC_6H_3\underline{p}\text{-}F)]BF_4 \cdot (CH_3)_2CO, \ \underset{\sim}{5b}$$
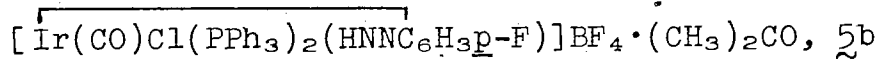
phenyl group in the acetatobis-[(2-phenylazo)phenyl]rhodium complex[63]. Further, N(1) shows a relatively short contact with the oxygen O(2) of the acetone molecule at 2.91Å, indicative of weak hydrogen bonding (Diagram III-2.); H(1) is approximately coplanar with the acetone molecule.

Protonation of the coordinating nitrogen atom of an arylazo group has been confirmed (mainly from n.m.r. evidence) in two cases,[5,108,140] and strongly indicated in others[90-92,109]. For example, Parshall[4,5] has reported the insertion of p-$FC_6H_4N_2^+$ into a Pt-H bond to give $[Pt(NH=NC_6H_4F)Cl(PEt_3)_2]^+$; Toniolo and Eisenberg[90] used a similar procedure to obtain $[IrH_2(NH=NC_6H_4NO_2)(PPh_3)_3]^+$, and Shaw[91] achieved insertion of $C_6H_5N_2^+$ into a Ru-H bond to obtain $[Ru(NH=NC_6H_5)Cl(CO)_2(PPr_2^nBu^t)_2]^+$. Similarly, Caglio[92] synthesised $[Ir(NH=NC_6H_4 p\text{-}R)H_2(PPh_3)_3]^+$ from $[IrH_3(PPh_3)_3]$ and p-$RC_6H_4N_2^+$ ($R=OCH_3$, NMe_2, Me). These findings provide further evidence that the position of protonation in the present compound, $\underset{\sim}{5b}$, is correctly established.

D. Properties

1. General Properties

The cationic ortho-metalated diimide complexes $[IrA(CO)(NH=NC_6H_3R)(PPh_3)_2]Y$ ($\underset{\sim}{5a}$-u) are crystalline solids varying in colour from yellow to yellow-orange.[a] They are stable over long periods to air, and appear to be stable to moderate heating (up to ca. 180°C). Although the extent of solubility

a. The complex $\underset{\sim}{5k}$ ($R=o$-NO_2) is violet in colour.

Table III-2.

Molar Conductances (Nitromethane, 25°C) and pKa
Values (Ethanol, 25°C) of Some Aryldiimide
Complexes [IrA(CO)(NH=NC$_6$H$_3$R)(PPh$_3$)$_2$]Y

Compound				Conductance Data		pKa
No.	A	R	Y	Molar Concentration	$\Lambda_M$ohm^{-1}mole^{-1}cm^2	
5b	Cl	p-F	BF$_4$	8.4 x 10^{-5}	123	
5ℓ	Cl	m-CH$_3$	BF$_4$			6.3
5j	Cl	o-Br	BF$_4$	1.7 x 10^{-4}	126	6.6
5r	F	o-Br	BF$_4$	1.6 x 10^{-4}	139	6.5
5s	I	o-Br	BF$_4$	1.8 x 10^{-4}	131	6.9
5t	Br	o-Br	BF$_4$	1.8 x 10^{-4}	128	
5u	OClO$_3$	o-Br	BF$_4$	4.0 x 10^{-4}	124	6.8

varies somewhat with the ring substituent, R, the complexes are
all soluble in methanol, ethanol, acetone, acetonitrile, chloro-
form, dichloromethane, and insoluble in diethyl ether, hexane,
pentane, water and benzene (the complexes obtained from benzene
solution during work-up of the reaction mixture appear not to
be capable of re-dissolving in benzene). The conductance of
the aryldiimide complexes in nitromethane solution is typical
of 1:1 electrolyte behaviour[44], as demonstrated for a few repre-
sentative compounds in Table III-2. Also listed in Table III-2
are some pKa values, illustrating the acidic nature of the
diimide hydrogen of the complexes. Magnetic susceptibility
measurements showed the aryldiimide complexes to be diamagnetic.

2. Infrared Spectroscopy

The positions of the carbonyl and azo-function stretches
(ν_{CO} and ν_{N_2}, respectively) for the aryldiimide complexes, 5a-u,
are listed in Table III-3. The i.r. spectrum of the p-bromophenyl-
diimide complex 5e, as illustrated in Diagram III-3, typifies
the complexes 5a-t having the tetrafluoroborate anion, whereas
Diagram III-4 shows the region of the spectrum of 5u having
bands assignable to the perchlorate anion and a perchlorato ligand.
In the i.r. spectra of all the complexes, 5a-u, the N-H
stretching frequency appeared in the region 3150-3180 cm^{-1}.
Those bands characteristic of the substituent, R, on the aryl-
azo ring were observable, except for R = Cl or Br. In all

Table III-3.

Some Infrared Spectral Data for the Aryldiimide
Complexes, $[IrA(CO)(NH=NC_6H_3R)(PPh_3)_2]Y^{(e)}$, 5a-u

Compound			Position of Absorption[f]	
No	R	A	$\nu_{CO}(\pm\ 1\ cm^{-1})$	$\nu_{N_2}(\pm\ 1\ cm^{-1})$
5a	H	Cl	2048	1410
5b	p-F	Cl	2048	1419
5c	p-Cl	Cl	2048	1409
5d	p-CH₃	Cl	2050	1410
5e	p-Br	Cl	2050	1410 [a][c]
5f	p-NO₂	Cl	2058	1408
5g	p-CF₃	Cl	2060	1403
5h	o-F	Cl	2065	
5i	o-Cl	Cl	2066	1443 [b]
5j	o-Br	Cl	2068	1442 [b][d]
5k	o-NO₂	Cl	2072	
5ℓ	m-CH₃	Cl	2051	
5m	m-OCH₃	Cl	2061	
5n	m-Br	Cl	2066	
5o	m-Cl	Cl	2068	
5p	m-NO₂	Cl	2072	
5q	m-F	Cl	2075	
5r	o-Br	F	2056	
5s	o-Br	I	2063	
5t	o-Br	Br	2067	
5j	o-Br	Cl	2068	1442 [b][d]
5u	o-Br	OClO₃	2093	

(a) Observed in both i.r. and Raman spectra.
(b) Observed in Raman spectrum only.
(c) Shifted to 1397 cm⁻¹ on ¹⁵N substitution of the Ir-bonded
    nitrogen atom.
(d) Shifted to 1426 cm⁻¹ on ¹⁵N substitution of the Ir-bonded
    nitrogen atom.
(e) 5a-t, Y = BF₄; 5u, Y = ClO₄
(f) KBr pellet.

Wavenumber, cm^{-1}

Absorbance
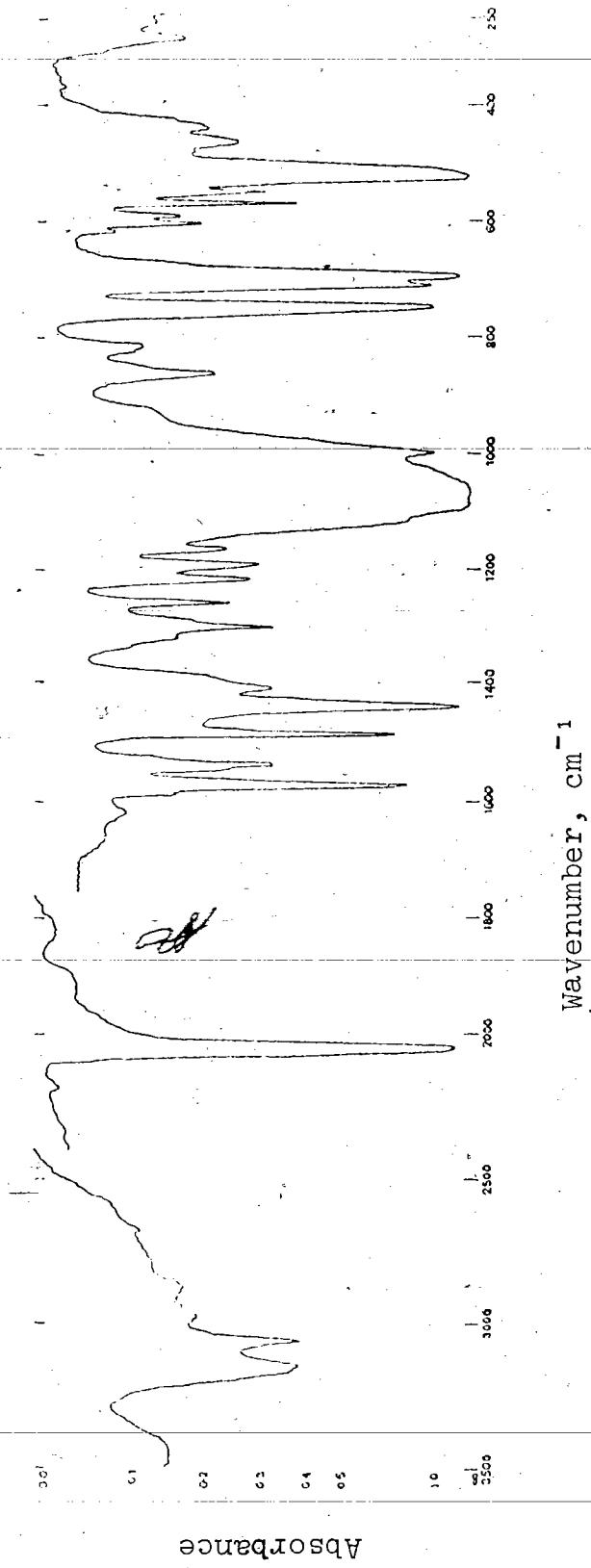
Diagram III-3.   Infrared spectrum of [Ir(CO)Cl(PPh$_3$)$_2$(HNNC$_6$H$_3$p-Br)]BF$_4$, 5e

cases, the absorptions due to the ring C-H bending modes of the triphenylphosphine ligands appeared at ca. 700 and 750 cm^{-1}.

Apart from the characteristic substitution patterns provided by the C-H bending modes of the Ir-bonded arylazo ring (as recorded in Table III-4), no definitive assignment of bands characteristic of ortho-metalation in the complexes 5a-u has been made, although such bands, lying in the region of ca. 1000-1100 cm^{-1}, have been claimed for other ortho-metalated complexes[95,78,81,93,94]. The assignment of bands in this region (1000-1100 cm^{-1}) to an ortho-metalated ring in the complexes 5a-u is not tenable owing to (a), the presence of a strong, broad band centred at ca. 1060 cm^{-1} and due to BF$_4^-$ or ClO$_4^-$, and (b), a strong absorption at ca. 1100 cm^{-1} in Vaska's complex (1) itself, a compound which is not known to contain an ortho-metalated phenyl ring. In fact, the results in Table III-4 for the meta-substituted compounds 5l-q even cast some doubt on the assignments based on the C-H bending ring-substitution pattern in the 700-900 cm^{-1} region. These results suggest that the sterically more crowded isomer A predominates over the sterically more favoured isomer B (see Figure III-3).

Isomer A

Isomer B
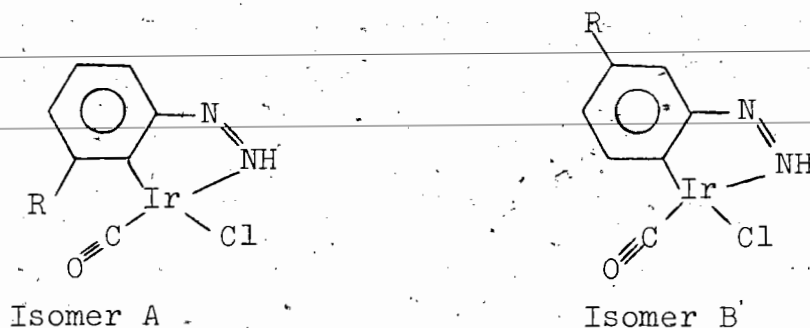
Fig. III-3

Table III-4.

Infrared C-H Bending Ring Substitution Patterns
of the ortho-Metalated Ring in the Aryldiimide Complexes,
$[IrA(CO)(NH=NC_6H_3R)(PPh_3)_2]Y$, 5a-u.[d]

Compound		Position of Absorption (cm^{-1})[c]		Comment
No.	R	Literature Value[a]	Observed Value	
5a	H	750	–	Masked by strong PPh$_3$ bands at 700 and 750 cm^{-1}
5b	p-F	830, 880	825, 875	
5c	p-Cl	" "	820, 870	
5d	p-CH$_3$	" "	810	
5e	p-Br	" "	830, 880	
5f	p-NO$_2$	" "	840, 890	
5g	p-CF$_3$	" "	840, 885	
5h	o-F	780	785	
5i	o-Cl	"	795	
5j	o-Br	"	790	
5k	o-NO$_2$	"	800	
5r	o-Br	"	775	
5s	o-Br	"	770	
5t	o-Br	"	770	
5u	o-Br	"	770	
5l	m-CH$_3$	780 or 830,880[b]	780, 830, 880	Mixture of isomers A and B[b]
5m	m-OCH$_3$	" " " "	785	Isomer A[b]
5n	m-Br	" " " "	790	Isomer A[b]
5o	m-Cl	" " " "	790	Isomer A[b]
5p	m-NO$_2$	" " " "	835	Probably isomer B[b]
5q	m-F	" " " "	795	Isomer A[b]

(a) Approximate values. See Reference 38.
(b) Two isomeric structures, A and B, are possible for the meta-substituted diimide complexes, 5l-q. See Figure III-3.
(c) KBr pellet.
(d) A and Y are as previously designated (see, e.g., Table III-3)

4. An absorption due to the N=N stretching frequency ν_{N_2}, could be assigned to only a few of the aryldiimide complexes, namely 5a-g and 5i-j, and in these cases the i.r. absorption (1403 to 1443 cm^{-1}) was invariably weak. The remaining complexes 5h, 5k and 5l-u, exhibited no i.r. absorptions assignable to ν_{N_2} and, further, underwent decomposition in the Raman He/Ne laser beam. By using the isotopically substituted diazonium salts $[RC_6H_4{}^{14}N\equiv{}^{15}N]^+BF_4{}^-$ (R = p-Br, o-Br) prepared by diazotisation of the corresponding aniline with $Na^{15}NO_2$, the isotopically substituted analogues of 5e and 5j were synthesised and investigated by Raman and (in the case of 5e) i.r. spectroscopy (c.f., Table III-3). In this way it was possible to assign absorptions to the N=N stretching frequencies. In view of (a) the uncertainty of the exact N=N stretching frequencies as determined by the i.r. absorptions in the solid state (KBr), (b) the apparently small differences in the ν_{N_2} values on varying the para-R substituent and (c) the possibility of coupling of the N=N and aromatic C=C stretching frequencies, caution should be exercised in attempting to draw any firm correlation between ν_{N_2} and the nature of the R substituent.

The i.r. spectra of all the aryldiimide complexes exhibit an absorption due to a terminal carbonyl stretching frequency in the region 2048-2093 cm^{-1} (c.f. Table III-3). Four separate series of complexes can be considered, all pertaining to the general formula $[IrA(CO)(NH=NC_6H_3R)(PPh_3)_2]Y$, viz:

Series (1)   Compounds 5b-g, Table III-3.
              R = para-substituent; A = Cl; Y = BF$_4$

Series (2)   Compounds 5h-k, Table III-3
              R = ortho-substituent; A = Cl; Y = BF$_4$

Series (3)   Compounds 5l-q, Table III-3
              R = meta-substituent; A = Cl; Y = BF$_4$

Series (4)   Compounds 5j and 5r-u, Table III-3
              R = o-Br; A = F, Cl, Br, I or OClO$_3$; Y = BF$_4$ or
              ClO$_4$

Within each of the series (1), (2), and (3), ν_{CO}

increases as the electron acceptor ability of the ring substi-

tuent, R, increases; thus, the bidendate aryldiimide ligand is

competing with the CO ligand for a share in the electron density

on the iridium. On consideration of the structure of the

diimide complex, (Figure III-4) it is seen that both the bi-

dentate ligand and the CO ligand lie in the equatorial plane of

the octahedron, and that the bonding of the terminal N atom of

the diimide ligand to the metal is trans to the CO ligand.

Back donation from a filled d$_\pi$-orbital of iridium into an empty
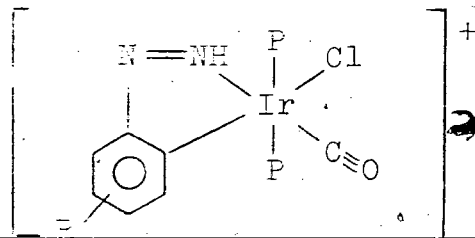
Fig. III-4 (P=PPh$_3$)

antibonding P_π-orbital of the nitrogen ligand should be facili-
tated by electron withdrawing substituents on the aryl ring of
the ligand. As the metal electrons are increasingly more
efficiently siphoned-off to the diimide ligand by the stronger
electron-withdrawing ring substituents, the back donation from
iridium to an empty antibonding P_π-orbital of the carbon monox-
ide diminishes, and ν_{CO} increases. Also, this effect should
result in a decrease in ν_{N_2} with increasing electron-acceptor
power of the ring substituent, R: the increased occupancy of
the nitrogen antibonding P_π-orbital results in a lowering of
the N=N bond order, and a decrease in the bond frequency (or
energy). This effect is exemplified by the ν_{CO} and ν_{N_2} values
for the para-substituted aryldiimides, 5b,c,e,f,g (Table III-5)
where it is seen that, as the electron withdrawing power of the
para-substituent increases, ν_{CO} increases and ν_{N_2} decreases.
Table III-5 lists, in addition to other parameters, the values
for the ratios $\nu_{N_2}/\nu_{N_2}+$, where ν_{N_2} applies to the aryldiimide
complex carrying an R substituent, and $\nu_{N_2}+$ to the similarly
substituted diazonium salt. The value of $\nu_{N_2}/\nu_{N_2}+$ also
decreases with increasing electron withdrawing power of R. This
decrease in $\nu_{N_2}/\nu_{N_2}+$ lends support to the mechanism just dis-
cussed. Thus, if the arylazo unit withdraws π-electrons from
the metal, then one would expect electron withdrawing para-
substituents to give relatively larger decreases in ν_{N_2} for the
complexes than the decrease in $\nu_{N_2}+$ observed for the correspond-

Table III-5.

A Comparison of ν_{CO} and ν_{N_2} of Some Aryldiimide Complexes $[IrCl(CO)(NH=NC_6H_3R)(PPh_3)_2]BF_4$ with the Hammett Substituent Constants (σ_p) of the R Substituents.

Compound No. R	ν_{CO}[a] ($\pm$ 1 cm^{-1})	σ_p	ν_{N_2}[a] ($\pm$ 1 cm^{-1})	$\nu_{N_2}{}^+$[a][b] ($\pm$ 1 cm^{-1})	$\nu_{N_2}/\nu_{N_2}{}^+$
5b p-F	2048	0.06	1419	2297	.618
5c p-Cl	2048	0.23	1409	2295	.614
5e p-Br	2050	0.23	1410	2291	.616
5f p-NO$_2$	2058	0.78	1408	2308	.610
5g p-CF$_3$	2060	0.54	1403	2310	.607
5i o-Cl	2066	–	1443	2295	.629
5j o-Br	2068	–	1442	2293	.629

(a) KBr pellet
(b) Applies to the aryldiazonium salt $R-\!\!\bigcirc\!\!-N\equiv N^+ \; BF_4^-$ used in the synthesis of the respective complex (5).

ing diazonium salts, due to the added drain of metal electrons into the N=N function; that is, $\nu_{N_2}/\nu_{N_2}+$ should decrease as the electron withdrawing power of R increases, as is observed.

For the o-chloro and o-bromo substituted complexes (5i and 5j, respectively), both the ν_{CO} and ν_{N_2} values are higher than for the corresponding p-chloro and p-bromo analogues (5c and 5e, respectively), as noted in Table III-5. This probably reflects a greater removal of electron density from iridium when the substituent is o than p, resulting in decreased back-donation to both the carbonyl and aryldiimide ligands. The origin of this effect is not clear, but may be due to a different sigma withdrawal through the Ir-C (aryl) bond. For the o-R series, as for the p-R series, ν_{CO} again increases as the electron withdrawing power of R increases. Owing to the lack of ν_{N_2} values for the o-R series, other than for 5i and 5j, the variation of ν_{N_2} with R is not known, but would be expected to parallel the p-R series (i.e., ν_{N_2} decreases as the electron withdrawing power of R increases).

In the ortho-bromophenyldiimide complexes 5j and 5r-u (c.f. Series 4, page 56) in which the ligand A is varied from F through I, Cl, and Br to $OClO_3$, the trend is for ν_{CO} to increase; the same trend is apparent in the related analogues of Vaska's complex[95] 1a-d (Table III-6) from which the diimide complexes 5r-u are synthesised. It is perhaps of some interest to note that ν_{CO} appears to be more sensitive to the effect of

Table III-6.

Carbonyl Infrared Stretching Frequencies (ν_{CO})
for the Complexes $[IrA(CO)(PPh_3)_2]$, 1, 1a-d,
and
$[\overline{IrA(CO)(NH=NC_6H_3Br-\underline{o})(PPh_3)_2}]Y^{(a)}$, 5j, 5r-u.

Compound No. A	$\nu_{CO}^{(c)}$ ($\pm$ 1 cm^{-1})	$\Delta\nu_{CO}^{(b)}$	Compound No. A	$\nu_{CO}^{(d)}$ ($\pm$ 1 cm^{-1})	$\Delta\nu_{CO}^{(b)}$
1a F	1957	8	5r F	2056	12
1 Cl	1965	0	5j Cl	2068	0
1b Br	1966	-1	5t Br	2067	1
1c I	1967	-2	5s I	2063	5
1d OClO$_3$	1982	-17	5u OClO$_3$	2093	-25

(a) 5j, r, t, s: Y = BF$_4$; 5u: Y = ClO$_4$

(b) $\Delta\nu_{CO} = (\nu_{CO})_{Cl} - (\nu_{CO})_A$, where A = F, Br, I, ClO$_4$

(c) In CHCl$_3$ (See Reference 95)

(d) KBr pellet

varying the anionic ligand A in the diimide series $5r-u$ than in the "Vaska's" series $1a-d$, as represented by the $\Delta\nu_{CO}$ values in Table III-6. This is particularly evident for A = $OClO_3$. A rationalisation of this observation is considerably hindered by the many factors involved in going from a four-coordinate, square-planar, molecular, d^8 system in which the A and CO ligands are mutually _trans_, to a six-coordinate, octa-hedral, cationic, d^6 system in which the A and CO ligands are _cis_ to one another. The effect on ν_{CO} of varying A in the complexes $1a-d$ is undoubtedly due to the _trans_ effect, which has been well established for square complexes, and particu-larly for $d^8(Pt^{II})$ complexes[96,97]. The _trans_ effect is gener-ally of less importance in octahedral complexes, and the variation of ν_{CO} with A in $5r-u$ may simply represent a manifes-tation of the _cis_ effect which is known to occur in certain octahedral, d^6 complexes[98]. It should be noted that complex $5j$, in which A = Cl, has BF_4^- as a counter ion, whereas $5u$, in which A = $OClO_3$, has ClO_4^- as the counterion. The nature of the counterion can affect both the intensity and the frequency of the i.r. bands, particulary for solid state spectra[98]. This in itself could account for $\Delta\nu_{CO}$ of $5u$ being greater than that of $1d$.

In the series, 1, $1a-d$ and $5j$, $5r-u$, it would be expected, purely on the basis of Pauling electronegativities, that ν_{CO} should decrease in the order of A = F > Cl > Br > I. However,

Table III-7.

Carbonyl Infrared Stretching Frequencies (ν_{CO})
for the Complexes [IrA(CO)(PPh$_3$)$_2$]($\underset{\sim}{1}$,1a-d) and
[$\overline{IrA(CO)(NH=NC_6H_3Br\text{-}o)(PPh_3)_2}$]Y[a] ($\underset{\sim}{5j}$, r-u) and
Electronegativities (X_A), Total Electronegativities (X_T)
and π-Electronegativities (X_π) of the Anionic Ligands, A.

Compound No. A	ν_{CO}[b] $\pm1cm^{-1}$	X_A[d]	X_T[d]	X_π[d]	Compound No. A	ν_{CO}[c] $\pm1cm^{-1}$	X_A	X_T	X_π
1a F	1957	4.02	4.02	0	5r F	2056	4.02	4.02	0
1 Cl	1965	2.94	4.19	1.25	5j Cl	2068	2.94	4.65	1.71
1b Br	1966	2.58	4.21	1.63	5t Br	2067	2.58	4.59	2.01
1c I	1967	2.22	4.24	2.02	5s I	2063	2.22	4.34	2.11
1d OClO$_3$	1982	3.70	4.62	0.92	5u OClO$_3$	2093	3.70	6.85	3.15

(a) $\underset{\sim}{5j}$,r,t,s: Y = BF$_4$. $\underset{\sim}{5u}$: Y = ClO$_4$

(b) In CHCl$_3$ (see Reference 95)

(c) KBr pellet

(d) See Appendix B for explanation and calculation

the actual order observed, namely, Cl ~ Br > I > F is contrary to this, placing F out of line. The explanation for this is that, in addition to their "sigma electronegativity", Cl, Br and I, but not F, can also exert a "pi-electronegativity" by accepting charge from the metal into their empty, low-lying d-orbitals. This variation of ν_{CO} with A was utilised by Vaska[95] to quantitatively estimate, from the ν_{CO} values, the total electronegativity (X_T), and hence the π-electronegativity (X_π) of a wide range of anionic ligands (A) in the complexes [MA(CO)(PPh$_3$)$_2$] (M = Ir, Rh). His values for X_A ("sigma" electronegativity), X_T and X_π for the complexes having M = Ir and A = F, Cl, Br, I and OClO$_3$, i.e., 1, 1a-d, are given in Table III-7 along with the corresponding values for the diimide series 5j, r-u. The definitions and methods of calculation of X_A, X_T and X_π are given in Appendix B. There is an immediately obvious discrepancy between the X_π values for 5u and 1d, in that the value for 5u is apparently too high. The explanation for this is not obvious, and may again be due to a number of factors in going from a square, molecular d^8 complex to a distorted octahedral, cationic d^6 complex, as previously discussed.

The ortho-bromophenyldiimide complex 5u, containing per-chlorate as both an anion and a ligand, is formulated as [IrOClO$_3$(CO)(NH=N=C$_6$H$_3$Br-o)(PPh$_3$)$_2$]ClO$_4$ on the basis of its elemental analysis (Table III-1), molar conductance (Table III-2),
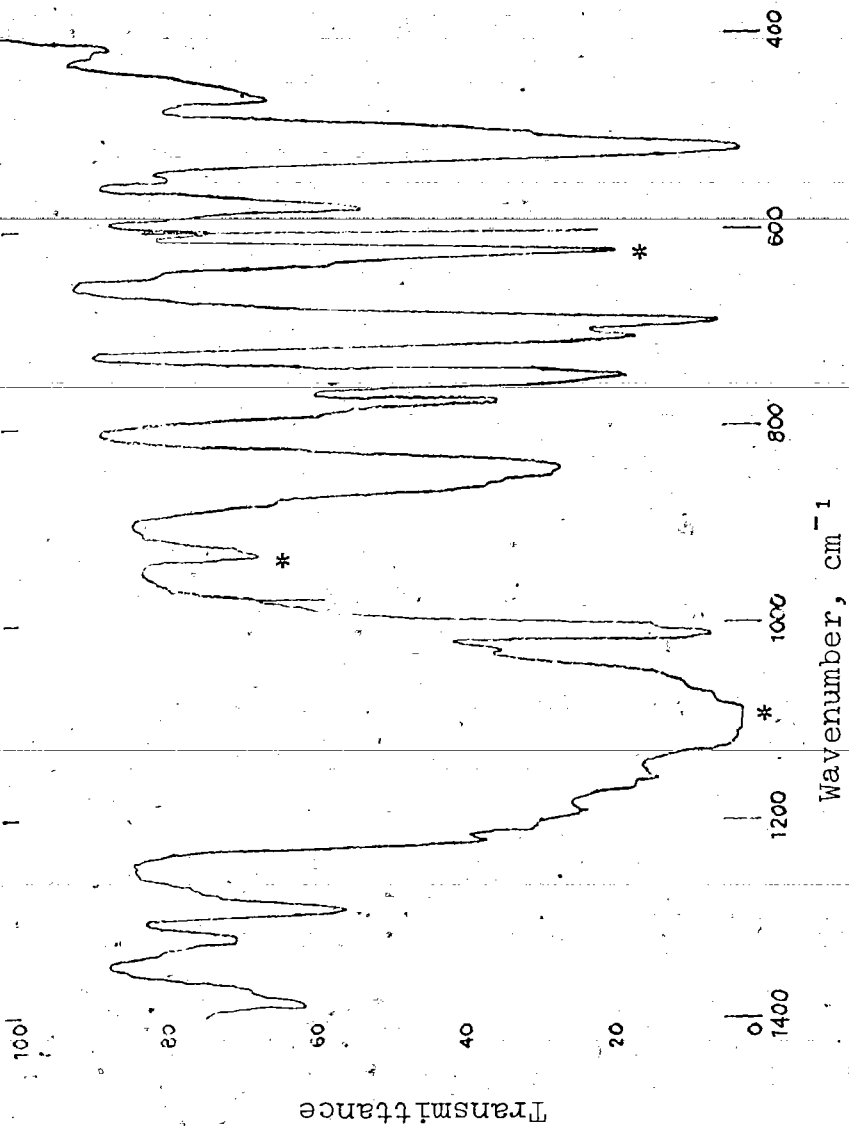
Diagram III-4. Region of infrared spectrum of [Ir(CO)(OClO$_3$)(PPh$_3$)$_2$(HNNC$_6$H$_3$O—Br)]ClO$_4$, 5μ, showing bands (*) indicative of OClO$_3$ (625, 932 cm^{-1}) and ClO$_4^-$ (625, ∼1100 cm^{-1}).

diamagnetism, and infra-red spectrum (Diagram III-4). The literature contains both i.r.[99,100] and X-ray[101-3] structural evidence for coordinated perchlorate complexes, and i.r. data for the uncoordinated perchlorate anion has been discussed by Nakamoto[39] and Cohn[103]. The uncoordinated perchlorate anion is a tetrahedral XY_4 molecule having four normal modes of vibration, $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(T_2)$ and $\nu_4(T_2)$ of which ν_3 and ν_4 are both i.r. and Raman active, ν_1 and ν_2 being Raman active only (no Raman data are available for $\underset{\sim}{5}u$ owing to its decomposition in He/Ne laser radiation). The bands ν_3 and ν_4 are observed in $KClO_4$ at 1140 and 624 cm^{-1}, respectively[103]. The relevant i.r. data for complex $\underset{\sim}{5}u$ and some other complexes containing both the free ClO_4^- anion and coordinated PPh_3 are listed in Table III-8. In all cases the ν_3 and ν_4 bands are observed, but ν_3 is close to a strong PPh_3 absorption at ca. 1100 cm^{-1}, resulting in a broad band in this region. The perchlorate anion can coordinate either as a monodentate ligand ($O-ClO_3$; C_{3V} symmetry) or as a bidentate ligand (O_2-ClO_2; C_{2V} symmetry). Examples of both types are given in Table III-8. The vibrational modes for the free anion and the coordinated monodentate anion are listed in Table III-9; the bands due to the bidentate ligand occur generally in the same regions as the monodentate ligand (the monodentate ligand has six vibrational modes which are i.r. and Raman active, whereas the bidentate ligand exhibits nine modes, eight of which are i.r. active).

Table III-8.

Infrared Data for the Aryldiimide Complex
$[\overline{Ir(OClO_3)(CO)(NH=NC_6H_3Br-\underline{o})(PPh_3)_2}]ClO_4$, $\underline{5}u$, and
Other Complexes Having a Perchlorate Anion or a
Perchlorato Ligand.

Compound[a]	Infrared absorptions (cm^{-1}) due to the perchlorate group[b][c]	Reference
$[Ir(CO)L_3]ClO_4$	1100(vs,br), 620(ms)	104
$[Rh(CO)L_3]ClO_4$	1100(vs,br), 620(ms)	104
$[Ir(OClO_3)(CO)L_2]$	1160(m), 1130(s), 1050(ms), 920(w), 620(ms)	104
$[Ir(H)Cl(OClO_3)(CO)L_2]$	1140(m), 1112(s), 1090(m)	105
$[Co(OClO_3)(CO)_2L_2]$	1160(m), 1125(s), 1080(ms), 928(mw), 623(ms)	104
$[Ni(C_5H_5N)_4(OClO_3)_2]$	1133(s), 1032(s), 929(m)	106
$[Ni(C_5H_5N)_4(OClO_3)_2]$	1130, 1030, 932, 628, 614	107
$[Co(C_5H_5N)_4(OClO_3)_2]$	1130, 1030, 930, 623, 615	107
$[Cu(O_2ClO_2)_2]$	1350(vw), 1270-1245(s), 1130(s), 1030(vw), 948(s), 920(s), 665(m), 647(m), 624(m), 600(s), 497(m), 466 466(w)	99
$[Ir(OClO_3)(CO)(NH=NC_6H_3Br-\underline{o})L_2]ClO_4$[d]	1100(vs,br), 932(mw), 625(s)	This work

(a)   L = PPh_3

(b)   S = Strong; m = medium; w = weak; vs = very strong; ms = medium strong; mw = medium weak; vw = very weak; br = broad.

(c)   Nujol mull, unless otherwise stated.

(d)   KBr pellet.

Table III-9.

Infrared Vibrational Modes for the Uncoordinated
Perchlorate Anion and the Monodentate Perchlorate Ligand.

Uncoordinated Anion, ClO_4		Monodentate Ligand, $OClO_3$	
Vibrational Mode	Approximate Frequency (cm^{-1})	Vibrational Mode	Approximate Frequency (cm^{-1})
$\nu_3(T_2)$	1100	$\nu_1(A)$	1100
$\nu_4(T_2)$	620	$\nu_2(A_1)$	900
		$\nu_3(A)$	620
		$\nu_4(E)$	1130-1300 (varies)
		$\nu_5(E)$	600
		$\nu_6(E)$	520

Owing to triphenylphosphine bands, and combination bands, the spectrum of 5u (Diagram III-4) does not permit differentiation between a mono- and a bidentate ligand. However, bidentate binding where five bonding sites are already occupied is very unlikely. The i.r. spectrum does, however, allow assignment of both a free and a bound perchlorate anion, the broad band centred at 1100 cm^{-1} being indicative of the free anion; the band at 932 cm^{-1} being indicative of a perchlorate ligand, and a strong band at 625 cm^{-1} being indicative of both moieties.

3. Nuclear Magnetic Resonance Spectroscopy

The proton nmr spectra of the -Cl, p-Br and o-Br complexes, 5i, 5e and 5j (saturated acetone-d_6 solution at 60 and 100 Mc/sec with TMS as internal standard) all exhibited two signals in the region $\tau 2$ to $\tau 4$. The spectrum of 5e (Diagram III-5) for example, showed multiplet structure centred at $\tau 2.46$ due to aromatic protons, from which individual resonance due to the 1,2,4-trisubstituted aromatic ring was not distinguished. In addition, a weak signal occurred at $\tau 3.61$ having an integrated intensity corresponding to a single proton. No splitting of this signal was observed, but it did split into a doublet   ($\tau 3.46$ and $\tau 3.75$)   centered at $\tau 3.61$ on ^{15}N-substitution of the nitrogen atom bonded to iridium. On deprotonation with base,   the $\tau 3.61$ signal was
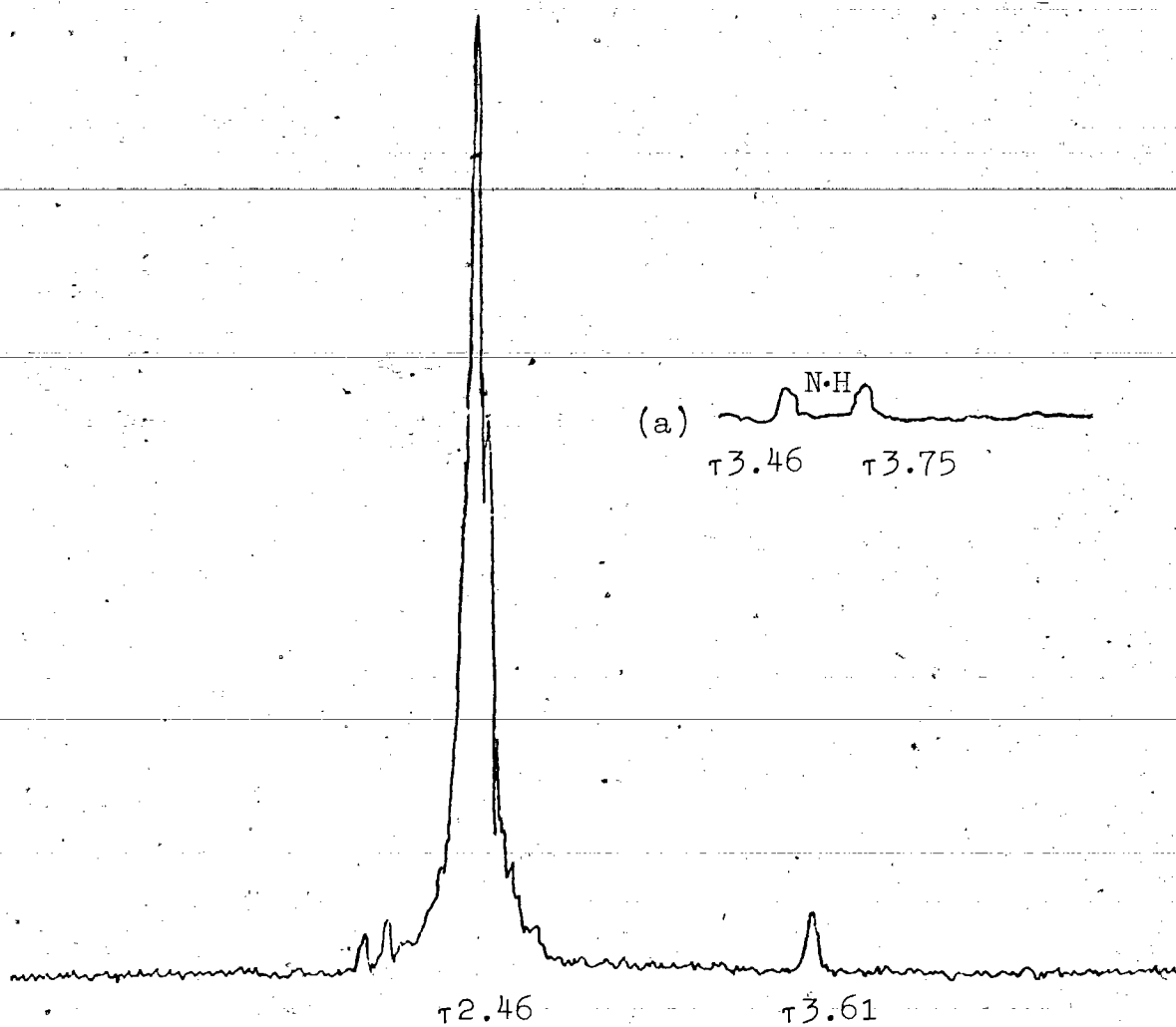
Diagram III-5.   Proton nmr spectrum of

[Ir(CO)Cl(PPh$_3$)$_2$(HNNC$_6$H$_3$p-Br)]BF$_4$, 5(e)
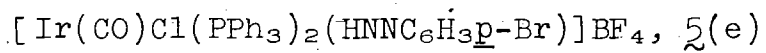
(a)   Splitting due to N^{15} substitution of nitrogen
atom bonded to iridium.

removed, re-appearing on addition of acid. This is in keeping

with the known reversible reaction of the aryldiimide complexes,

5, with base:

$$[\overline{IrA(CO)(NH:N-C_6H_3R)(PPh_3)_2}]Y \underset{\underset{(HY)}{Acid}}{\overset{Base}{\rightleftarrows}} [\overline{IrA(CO)(NNC_6H_3R)(PPh_3)_2}]$$

$$+ \quad HY$$
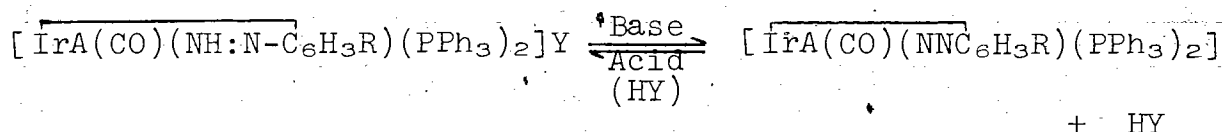
Similarly, the i.r. absorption at 3150 cm^{-1} attributable to the

N-H stretching frequency (Chapter III-D2) was removed by treat-

ment of the complexes 5 with base. Thus, assignment of this

signal at $\tau 3.61$ to an N-bonded proton seems to be quite logical,

yet it does exhibit some puzzling features. Neither exchange

nor a shift were observed in the nmr spectrum in the presence of

H_2O, D_2O or CF_3COOH, although the $\tau 3.61$ signal did disappear

with DBF_4 over a narrow range in the region of pH 5.7. Also,

the upfield position and low coupling constant $(J_{15_{N-H}})$ of 29 Hz

appear to be unusual. The corresponding values for somewhat

related compounds are given in Table III-10, but it should be

noted that no similar systems having the $-\overset{H}{N}=N-$ function as a

member of a five-membered metallocycle are available for com-

parison. It has been demonstrated[110,111] that the amount of s-

character of the nitrogen bond orbital should be linearly

related to the ^{15}N-H coupling constant by the relationship,

$s(\%) = 0.43 J_{(^{15}N-H)} - 6$. Thus, e.g., NH_4^+, an sp^3 system, has

$J_{(^{15}N-H)} = 73.2$ Hz and $s = 25\%$, and $(\emptyset)_2C = NH_2$, an sp^2 system,

has $J_{(^{15}N-H)} = 92.6$ Hz and $s = 33.3\%$. On this basis, the

Table III-10

Proton Nuclear Magnetic Resonance Data
for Aryldiimide Complexes

Compound	τ value for ^{14}N-H	$J(^{15}$N-H) (Hz)	Reference
$[PtCl(PEt_3)_2(NH=NC_6H_4p-F)]^+$	-5.1	77	5
$[Pt(PPh_3)_3(NH=NC_6H_4p-F)]^{++}$	+7.25		109
$[RuCl(CO)_2(PPr^n_2Bu^t)_2(NH=NC_6H_5)]^+$	-3.57		91
$[OsCl(FBF_3)(PPh_3)_2(NH=NC_6H_4p-Me)]$	-3.78	69.3	140
$[OsCl_2(CO)(PPh_3)_2(NH=NC_6H_4p-Me)]$	-3.50	67	140
$[RhCl_3(PPh_3)_2(NH=NC_6H_4p-Me)]$	-1.89	68	108,140
$[RhCl_3(PPh_3)_2(NH=NC_6H_4p-OMe)]$	-1.60	65	108,140
$[IrH_2(PPh_3)_2(NH=NC_6H_4p-NO_2)]^+$	-3.5		90
$[IrH_2(PPh_3)_2(NH=NC_6H_4p-OCH_3)]^+$	-3.2		92
$[IrCl(CO)(PPh_3)_2(NH=NC_6H_3p-Br)]^+$, 5e	+3.61(acetone-d_6) +3.67(CDCl$_3$)	29 39	This work
$[IrCl(CO)(PPh_3)_2(NH=NC_6H_3\underline{o}-Br)]^+$, 5j	+3.70(acetone-d_6)		This work
$[IrCl(CO)(PPh_3)_2(NH=NC_6H_3\underline{o}-Cl)]^+$, 5i	+3.14(acetone-d_6)		This work

nitrogen bond orbital (an sp^2 system, as demonstrated by the
Ir-N=N bond angle of 120° from the X-ray structural data on 5)
s-character of 6.5% as calculated from $J_{15_{N-H}} = 28$ Hz is
inordinately low. The low coupling constant might indicate
bonding of the proton to the nitrogen adjacent to the isotopi-
cally (^{15}N) substituted one (i.e., to the ring-bound nitrogen
atom), but this is essentially ruled out by the X-ray structural
data, as discussed earlier in Chapter III-D3. The chemical
shift and ^{15}N-H coupling constant are presumably influenced by
a combination of factors inherent in the structural features of
the ortho-metalated aryldiimide complex. That ortho-metalation,
resulting in incorporation of the protonated azo system into a
conjugated, five-membered, metal-containing ring may have a
strong influence is indicated by a comparison of the n.m.r.
data for 5e, 5i and 5j with that of the other complexes listed
in Table III-10. Further, the proximity of the N-H moiety to
the iridium may result in its experiencing an anisotropic field
effect exerted by the metal[32,112,113]. Hydrogen bonding
between the N-bonded proton and the solvent may also be a con-
tributing factor; an X-ray structural determination showed such
H-bonding to exist in the presence of acetone solvate molecules
(Chapter III-D3), and the n.m.r. data for 5e in Table III-9
indicates some solvent dependence on going from acetone-d_6 to
deutero chloroform.

In conclusion, a consideration of the n.m.r., i.r. and

X-ray structural data, along with the deprotonation of the

aryldiimide complexes by base, confirms the presence of a

proton on the azo function. The X-ray structural data, in

particular, favours its being on the iridium-bonded nitrogen,

and this is substantiated by earlier and current observations

of protonation of the coordinating nitrogen of an arylazo

group.[4,5,90-92,108,109,140,182]

4. Electronic Spectroscopy

The electronic spectra (Table III-11 and Diagram III-6)

of the aryldiimide complexes, $[IrA(CO)(NH=NC_6H_3R)(PPh_3)_2]Y$, in

ethanol solution showed bands in the visible region which, in

general, were broad, asymmetric and ill-defined. In all of the

spectra, two maxima, λ_1 and λ_2, in the regions 300-400 nm and

400-450 nm, respectively, with molar absorptivities, ϵ, of the

order of 10^3 could be approximately located. The complexes $\underset{\sim}{5}l$,

$\underset{\sim}{5}u$ and $\underset{\sim}{5}s$ (Table III-11) showed an additional weak band at ca.

500 nm, probably due to $N=N$ transitions; these three complexes

are an orange-yellow colour compared with the "pure" yellow of

the other aryldiimide complexes. The two higher energy bands

cannot be assigned with any certainty to specific transitions.

Thus, the magnitude of molar absorptivity(10^3) and the shift of

λ_1 to higher energy on changing the anionic ligand A from I to

Cl are consistent with both a d-d transition and metal→ligand

(diimide) charge transfer; the virtual invariance of ϵ with

Table III-11

Electronic Spectral Data for Some
Aryldiimide Complexes $[\overline{IrA(CO)NH=NC_6H_3R}(PPh_3)_2]Y$

Compound				Wavelength (λ, nm) and Molar Absorptivity (ϵ, $m^{-1}cm^{-1}$) Maxima [a][b]					
No.	A	R	Y	λ_1	ϵ_1	λ_2	ϵ_2	λ_3	ϵ_3
5e	Cl	p-Br	BF_4	340	7,260	400-450	1,210	-	0
5j	Cl	o-Br	BF_4	325	4,740	400-450	840	-	0
5ℓ	Cl	m-CH$_3$	BF_4	325	2,820	400-450	1,460	500	800
5j	Cl	o-Br	BF_4	325	4,740	400-450	840	-	0
5u	OClO$_3$	o-Br	ClO_4	340	4,500	400-450	1,480	500	100
5s	I	o-Br	BF_4	350	5,080	400-450	2,110	500	200

(a) In absolute ethanol at 25°C

(b) Approximate values.
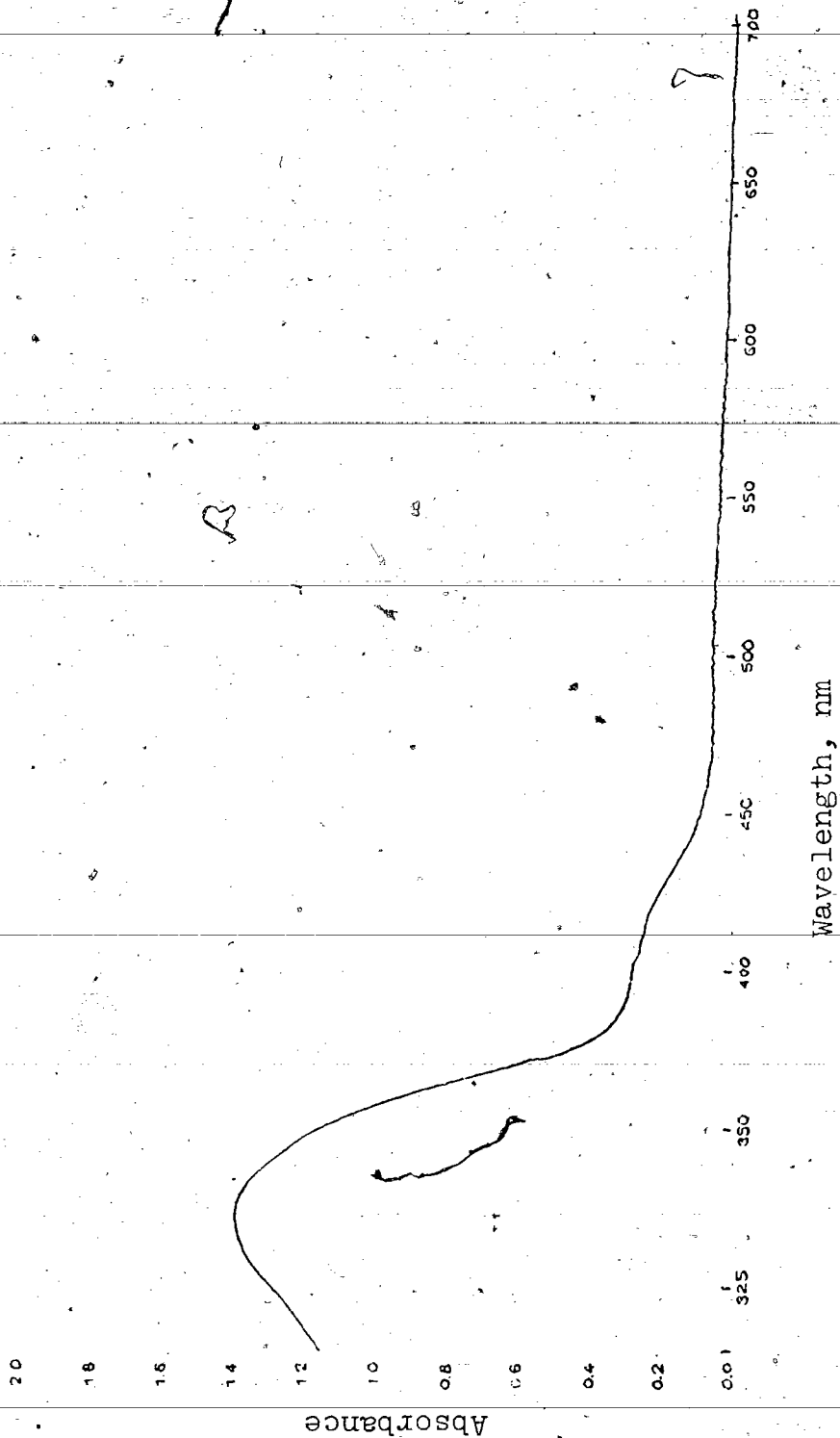
Diagram III-6. Visible spectrum of $[Ir(CO)Cl(PPh_3)_2(HNNC_6H_3p\text{-}Br)]BF_4$, $\underline{5}e$

changing A suggests, however, predominance of a d-d transition.

Again, on varying the ring substituent, R, the shift of λ_1 to

lower energy and higher molar absortivity as the electron-

acceptor power of R increases is consistent with a $\pi \rightarrow \pi^*$

transition and for metal → ligand (diimide) charge transfer.

Also, there is undoubtedly some contribution to this high

energy band from the partially overlapping aromatic band

(λ_{max} = ca. 260 nm).

The energy of the band at 400-500 nm (λ_2) appears to be

invariant to changing A or R, and is probably associated with

the metal rather than with the ligand.

A comparison of the spectra of the aryldiimide complexes

with those of Vaska's complex, 1, and the corresponding aryl-

tetrazene complexes, 4, revealed no region of absorption exclu-

sive to the aryldiimide complexes. Thus, visible spectroscopy

could not be utilized to ascertain the amount of aryldiimide

product formed in the reaction solutions, as was successfully

done in the case of the aryltetrazene syntheses (c.f., Chapter

II-D4).

E.   Discussion

As with the aryltetrazene complexes (4) the formation of

the aryldiimide complexes (5) from the reaction between a tran-

sition metal complex and an aryldiazonium salt is unique, and

again raises the question of their mode of formation. The most

obvious route would involve direct coordination of the aryl-diazonium cation, via its terminal nitrogen, to the iridium, affording the initially expected five-coordinate arylazo adduct, 2. ortho-Metalation, with concomitant protonation of the azo function would then follow, satisfying the tendency for Ir(III) to achieve six-coordination.

Another possibility takes into consideration the involvement of a common intermediate leading to both of the products (4 and 5) isolated from the reaction. In the discussion of the aryltetrazene complexes (Chapter II-E), the participation of an aryldiazene intermediate (ArN=NH) in the mechanistic route was indicated. This same intermediate could also lead to the aryldiimide complexes by formally bonding in a bidentate manner (as with the azobenzenes, ArN=NAr)[88] to the iridium. The mechanistic possibilities are discussed in detail in Chapter VII.

Two features of the aryldiimide complexes are worthy of note in connection with the nitrogenase model.

(1) ν_{N_2} occurs at ca. 1400 ~ 1450 cm^{-1} which represents a substantial lowering from the value (ca. 2300 cm^{-1}) in the diazonium salt, exceeding the lowering of ν_{N_2} observed for some complexes with bridging dinitrogen ligands[114].

(2) Spontaneous hydrogenation of the nitrogen function has occurred in the formation of the ortho metalated aryldiimide complexes. Thus, the equivalent of the diimide complex in Parshall's model[5,7,29] has been achieved in this case without
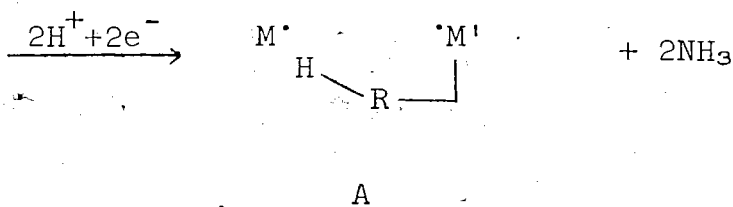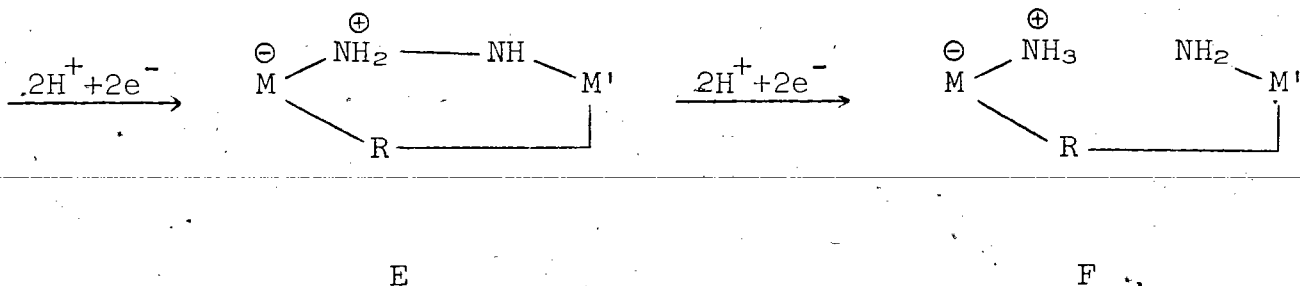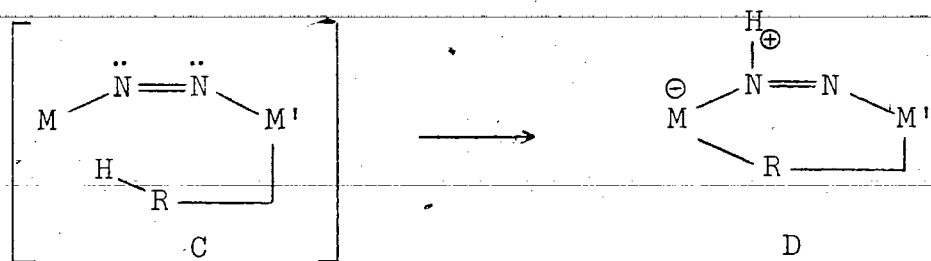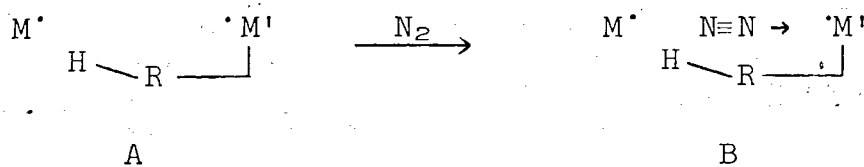
Fig. III-5

M·, ·M' do not necessarily signify metals possessing an unpaired electron, but signify the necessary availability of two non-bonded electrons required for the electron rearrangement B → C.

the participation of a metal hydride. Furthermore, the aryl-
diimide complexes undergo further hydrogenation under extremely
mild conditions (H_2, 1 atm., 25°C, $Pd/BaSO_4$) to yield the
arylhydrazine complexes, $[IrCl(CO)(H_2NHAr)(PPh_3)_2]BF_4$ (7).
The hydrogenation studies are discussed in Chapter V.

It is possible, therefore, that in nitrogenase, the
initial hydrogenation of the complexed dinitrogen molecule to
a diimide complex arises from a rearrangement involving C-H
bond cleavage, rather than the involvement of a metal hydride.
As mentioned previously (Chapter III-C) there are now numerous
examples of transition metal complexes involving coordination
from the ortho carbon of an aromatic ring[56-88] or from a
methylene group[115]. In all examples till now, however, the
eliminated hydrogen atom has either migrated to the metal to
form a hydride-complex, or has been removed completely, for
example, as hydrogen halide[79,88,116].

A suggested scheme is shown in Figure III-5. Here it is
envisaged that M' is bonded to a group RH which is oriented in
close proximity to M. Coordination of dinitrogen and electron
rearrangement to the intermediate C is followed by proton shift
to give the diimide complex D. An important feature in the
activation of the dinitrogen molecule towards further reduction
would be the possibility of electron delocalization in the
resulting cyclic complex leading to a reduced N=N bond order.

Reduction by 6e⁻ would lead directly to the formation of

NH_3 and regeneration of A. There are a number of obvious groups present in the enzyme which might fill the role of R-H in this model; as two examples, the conversion C → D could involve a cysteine residue:
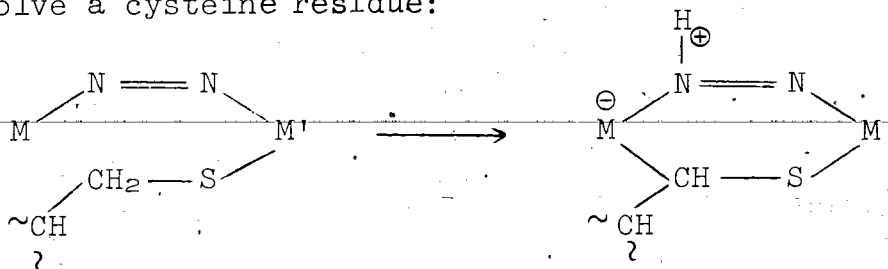
or a tyrosine residue:
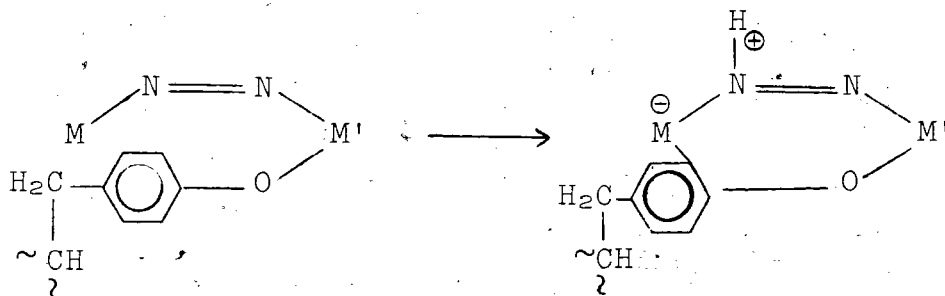
M and M' are most likely to represent the two metals, iron and molybdenum, necessary for nitrogen fixation. It should be kept in mind, however, that the ability to consume atmospheric nitrogen is not restricted to metallic systems, since instances of organic compounds exhibiting such behaviour are known[115,117]. Furthermore, dinitrogen is capable of bridging between a metal and a non-metal (for example, phosphorus) to give complexes with similar values of ν_{N_2} to the purely metal bridged complexes [114]. It would therefore be premature to rule out the possibility that dinitrogen is attached to a non-metal in the enzyme[118]. Thus, in the above examples, it is instead conceivable that

the dinitrogen is attached directly to the sulphur atom of the cysteine or to the oxygen of the tyrosine residue, without intervention of M'. The model would still apply, and the ring size would be smaller.

CHAPTER IV

Molecular ortho-Metalated Arylazo Complexes

A. Introduction

Investigation of the nature of the aryldiimide complexes, $[Ir(CO)A(PPh_3)_2(NHNAr)]Y$ (5a-u), as discussed in Chapter III, included their deprotonation with base to provide contributory evidence for the presence of a proton on the azo function. Reversible deprotonation of aryldiimide complexes had already been demonstrated by Parshall[4-6] for $[PtCl(PEt_3)_2(NHNAr)]^+$ and, more recently, has also been reported by Ibers[119], Robinson[108,140] and Cenini[109] for $[Ir(CO)Cl_2(PPh_3)_2(NHNPh)]^+$, $[RhCl_3(PPh_3)_2NHNAr]$ and $[Pt(PPh_3)_3(NHNAr)]^{2+}$, respectively. It is pertinent to note here one reported instance where deprotonation of an aryldiimide complex was not achieved with base.[92] Thus, the complex $[IrH_2(PPh_3)_3(NHNAr)]^+$ with alkalis gave the trihydride, $[IrH_3(PPh_3)_3]$, instead of the expected arylazo derivative, $[IrH_2(PPh_3)_3(N=NAr)]$.

It was found that methanol solutions of the complexes 5a-u on treatment with excess base immediately changed colour from yellow to pink. In the case of the para-bromo complex, 5e, the product was isolated as a pink solid and subsequently characterised as the molecular ortho-metalated arylazo complex 6; this deprotonation was found to be reversible, 6 being readily reconverted to 5e by treatment with HBF₄:

$$[\text{Ir(CO)Cl(PPh}_3)_2(\text{NHNC}_6\text{H}_3\underline{p}\text{-Br})]\text{BF}_4$$

$$\underset{\sim}{5e}$$

$$\text{HBF}_4 \;\big\Updownarrow\; \text{NaOH}$$

$$[\text{Ir(CO)Cl(PPh}_3)_2(\text{N=NC}_6\text{H}_3\underline{p}\text{-Br})] + \text{NaBF}_4 + \text{H}_2\text{O}$$

$$\underset{\sim}{6}$$
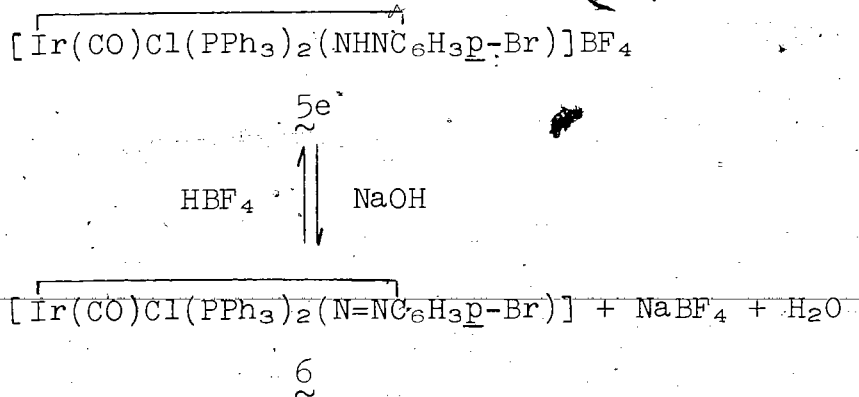
B. Synthesis

The molecular <u>ortho</u>-metalated <u>para</u>-bromophenylazo complex $\underset{\sim}{6}$ was readily precipitated as a pink solid in ca. 70% yield by the addition of a methanol-water solution of NaOH to a methanol solution of $[\text{Ir(CO)Cl(PPh}_3)_2(\text{NHNC}_6\text{H}_3\underline{p}\text{-Br})]\text{BF}_4$, $\underset{\sim}{5e}$. It was also prepared in slightly lower yield by utilising a methanol-water solution of sodium acetate or neat Et_3N in place of the NaOH solution, or by the addition of neat Et_3N to a suspension of $\underset{\sim}{5e}$ in diethylether. The product, $\underset{\sim}{6}$, analysed as 53.4% C; 3.4% H; 2.7% N; requiring 53.6% C; 3.6% H; 2.9% N.

The arylazo complex $\underset{\sim}{6}$ was reconverted in ca. 70% yield to the diimide complex $\underset{\sim}{5e}$ by the dropwise addition of a 48% aqueous HBF_4 solution to a suspension of $\underset{\sim}{6}$ in ethanol.

C. Properties

1. General Properties

The ortho-metalated arylazo complex $\underset{\sim}{6}$ is a pink, micro-crystalline, diamagnetic, air-stable solid, readily soluble in benzene, chloroform and dichloromethane, only slightly soluble in ethanol, methanol and diethyl ether, and insoluble in water and acetone.

2. Infrared Spectroscopy

The solid phase (KBr pellet) infrared spectrum of $\underset{\sim}{6}$, illustrated in Diagram IV-1, exhibited no frequencies attributable to either ν_{NH} or $\nu_{BF_4^-}$. The CO stretching frequency occurred at 2000 cm^{-1}. Absorptions due to the ring C-H bending modes of the triphenylphosphine ligands appeared at 685 and 745 cm^{-1}, while bands at 812 and 863 cm^{-1} can be assigned to the C-H bending modes of the 1,2,4-trisubstituted ortho-metalated arylazo ring. By using the isotopically substituted diazonium salt $[p\text{-}BrC_6H_4{}^{14}N\equiv{}^{15}N]^+BF_4^-$, prepared by diazotisation of p-bromoaniline with $Na^{15}NO_2$, the isotopically substituted analogue of $\underset{\sim}{6}$, $[Ir(CO)Cl(PPh_3)_2({}^{15}N=NC_6H_3p\text{-}Br)]$, was synthesised; the medium intensity i.r. band at 1450 cm^{-1} in the non-isotopically substituted complex shifted to 1413 cm^{-1} in the ^{15}N analogue, and was thus assigned to ν_{NN}. Attempted confirmation of ν_{NN} by Raman spectroscopy proved unsuccessful owing to decomposition in the He-Ne radiation.

Wavenumber, cm^{-1}
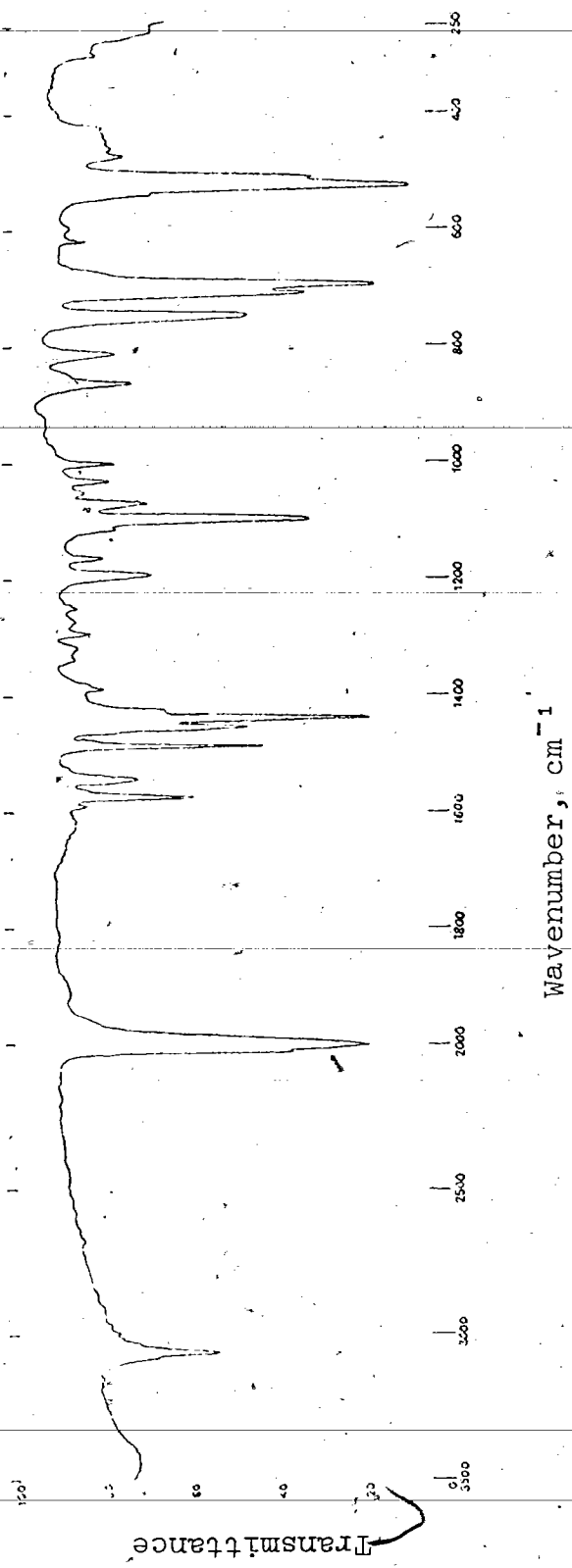
Diagram IV-1. Infrared spectrum of $[Ir(CO)Cl(PPh_3)_2(NNC_6H_3p\text{-}Br)]$, 6

Transmittance

Protonation of the molecular arylazo complex 6 to yield
the cationic aryldiimide complex 5e results in a decrease of
ν_{NN} (from 1450 cm^{-1} to 1410 cm^{-1}, respectively) and an increase
of ν_{CO} (from 2000 cm^{-1} to 2050 cm^{-1}, respectively), as depicted
below. That the lowering of ν_{NN} may be due to increased back-

ν_{CO}: 2000 cm^{-1} ν_{CO}: 2050 cm^{-1}

ν_{NN}: 1450 cm^{-1} ν_{NN}: 1410 cm^{-1}
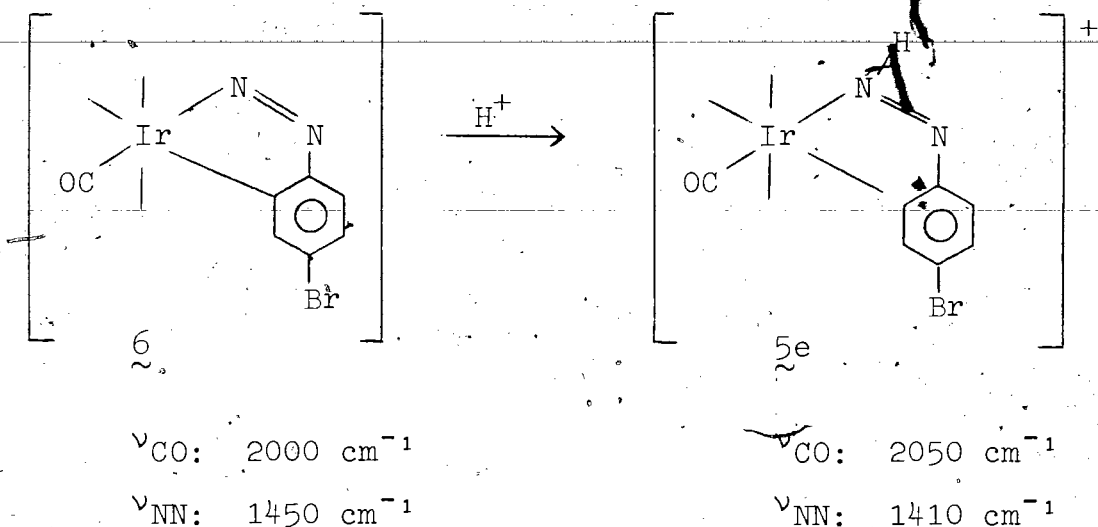
donation from a filled d_π-orbital of iridium to an empty anti-
bonding p_π-orbital of the nitrogen ligand in 5e is reflected
in the higher value of ν_{CO} for 5e, indicating decreased back-
donation from iridium to an empty antibonding p_π-orbital of the
carbon monoxide ligand.

3. Nuclear Magnetic Resonance Spectroscopy

The proton nmr spectrum of 6 (CDCl$_3$ solution at 100 Mc/
sec with TMS as internal standard) as illustrated in Diagram
IV-2 exhibited only two signals, both having multiplet struc-

τ 2.58   τ 3.17
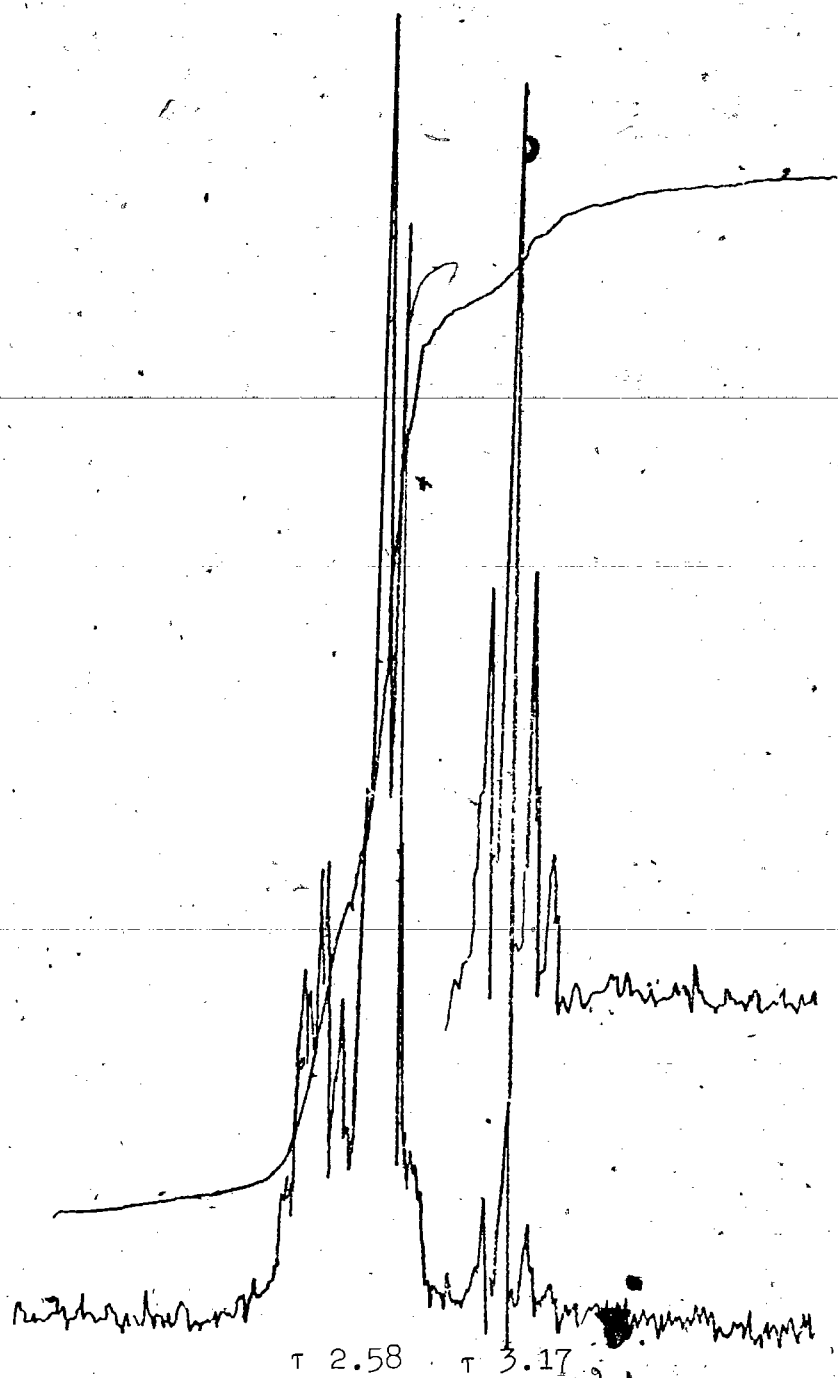
Diagram IV-2. Proton n.m.r. spectrum of

$[Ir(CO)Cl(PPh_3)_2(NNC_6H_3\underline{p}-Br)]$, 6
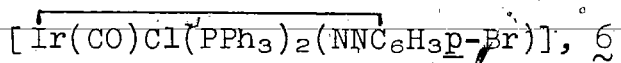
tures, centred at τ 2.58 and τ 3.17. The integrated intensity
of the τ 2.58 multiplet corresponds to 30 protons and is
ascribed to the triphenylphosphine protons, whereas the inte-
grated intensity of the τ 3.17 multiplet corresponds to three
protons and is ascribed to the protons of the ortho-metalated
ring.

A comparison of the proton nmr spectra of 6 and 5e
reveals one interesting feature, namely, the ability to distin-
guish ortho-metalation in the molecular arylazo complex 6, but
not in the cationic aryldiimide complex 5e. A probable explan-
ation for this is that protonation of the molecular complex 6
to yield the cationic complex 5e causes deshielding of the
protons of the ortho-metalated ring in 5e (relative to those in
6) resulting in a shift downfield to coincide with the signal
due to the triphenylphosphine protons. This is depicted dia-
gramatically below:
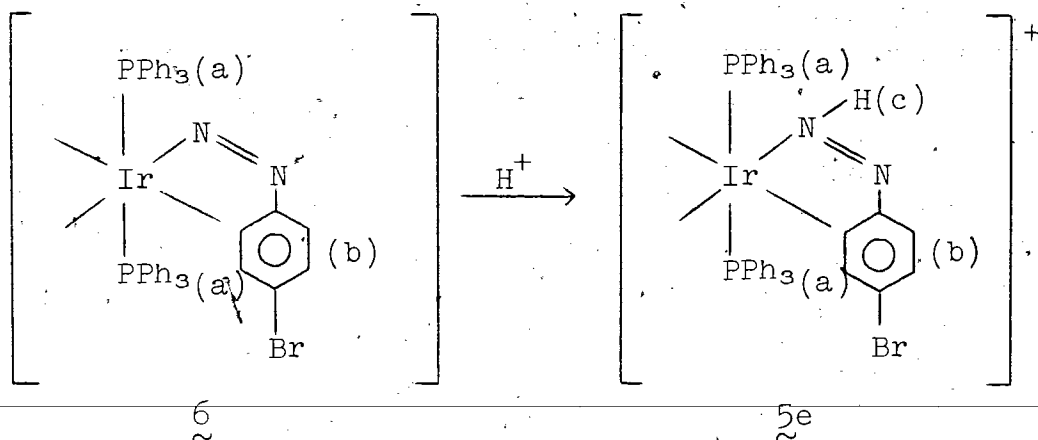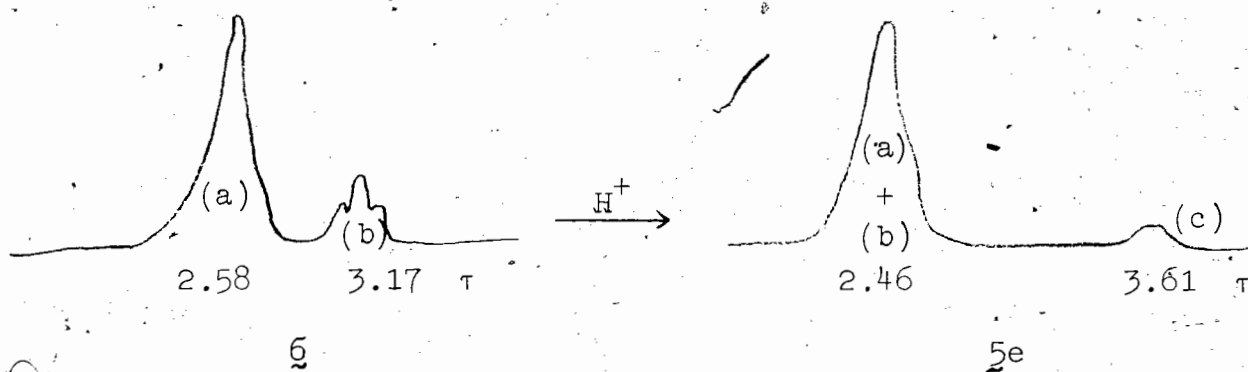
Such downfield shifts of the protons of a coordinated ligand occurring on conversion of molecular species to the cationic form have been reported in the literature. For example, the protonation of $[(C_p)Fe(CO)_2(C_3H_4)]$ to give $[(C_p)Fe(CO)_2(C_3H_5)]^+$ results in a downfield shift of the allyl signal from τ 5.1 to τ 4.02[120], and the conversion of $[(COD)PdCl_2]$ to $[(COD)PdCl]_2^{2+}$ by treatment with $Et_3O^+BF_4^-$ shifts the cyclooctadiene (COD) protons from τ 4.5 to τ 3.6[121].

CHAPTER V

Hydrogenation Studies on the Cationic ortho-Metalated

Aryldiimide Complexes, 5, the Molecular

ortho-Metalated Arylazo Complex, 6,

and the Aryltetrazene Complexes, 4

A. Introduction

As already briefly discussed in Chapter I, the mode of
biological reduction of N_2 to NH_3 by nitrogenase enzymes under
mild conditions is a problem still to be solved. One proposed
mechanism[12] invokes the initial coordination of N_2 to a metal
followed by step-wise two-electron reductions by way of

$$N_2 \xrightarrow{2e^-} N_2H_2 \xrightarrow{2e^-} N_2H_4 \xrightarrow{2e^-} 2NH_3.$$ However, the first

step in this reduction series is thermodynamically unfavourable,
being endothermic to the extent of 49 kcal mole^{-1} and therefore
not feasible under mild conditions[13,122,124]. To avoid this
unfavourable two-electron reduction to coordinated N_2H_2, Borodko
and Shilov[13] have proposed a four-electron reduction of N_2 to
coordinated $N_2H_2^{2-}$, the two additional electrons being trans-
ferred from the metal atom(s) constituting the complex.

The currently proposed model systems for nitrogenase
include dinitrogen[13,18-21], arylazo[5-7,140], aryldiimide[51,140]
and aryltetrazene[51] complexes, and of importance in each
instance is the feasibility of facile hydrogenation of their

azo (-N=N-) functions.

Although many metal dinitrogen complexes have now been isolated and studied, in no instance has the azo function been demonstrated to undergo facile hydrogenation. Despite the fact that ν_{N_2} in certain dinitrogen complexes has been lowered as far as 1630 cm^{-1} (from 2331 cm^{-1} in the uncoordinated N_2 molecule) by attachment of an acceptor atom M' to the terminal nitrogen atom to form a polynuclear M-N=N-M' bridge, such compounds have not been found to undergo reduction of the azo function[114,123]. Attempts to protonate and reduce mono-hapto-dinitrogen complexes have usually led to the protonation and oxidation of the metal with liberation of dinitrogen, some-times together with dihydrogen[128]. Recently, however, Chatt et al.[129] have successfully protonated, under mild conditions, the bis(mono-hapto-dinitrogen) complexes trans-$[M(N_2)_2(diphos)_2]$ (M = Mo or W, diphos = $Ph_2PCH_2CH_2PPh_2$)[130-132] with HX (X = Cl or Br) to yield $[MX_2(N_2H_2)(diphos)_2]$ and molecular nitrogen. Treatment of the tungsten complex (X = Cl) with sodium tetra-phenylborate afforded the 1:1 electrolyte $[WCl(N_2H_2)(diphos)_2]BPh_4$ in which the N_2H_2 ligand has been shown by X-ray diffraction analysis[133] to be present in the monohapto hydrazido (2-) form, viz., W=N—NH_2.

The behaviour of certain arylazo and aryldiimide complexes toward hydrogenation under mild conditions has been studied by various workers and the results are summarized in Table V-1.

Table V-1

A Summary of Hydrogenation Studies on Arylazo and
Aryldiimide Complexes.

Complex	$\nu_{NN}(cm^{-1})$	Conditions	Result	Ref.
I [PtCl(PEt$_3$)$_2$(NNAr)]	1440-1463	H$_2$/Pt 1 atm, 25°C	Hydrazine complex[a]	4,5, 6,7
II [(Cp)Mo(CO)$_2$(NNAr)]	1545-1562	(b)	Hydrogenation occurred[b]	3,4, 125
III [Pt(PPh$_3$)$_2$(NNSO$_2$Ph)$_2$][c]	1450-1480[d]	H$_2$/Pd, 5 atm, 60°C prolonged	PhSO$_2$NH$_2$ [Ptµ$_2$(PPh$_3$)$_2$][e]	37
IV [RhCl$_2$(PPh$_3$)$_2$(NNPh)]	1614 and 1549	H$_2$,1 atm, 60°C,CHCl$_3$	[RhCl$_3$(NH$_2$NHAr)- (PPh$_3$)$_2$]$_2$	108,134 140
V [HB(Pz)$_3$Mo(CO)$_2$(NNPh)][f]	1559[g]	H$_2$/Pt[h]	N=N not reduced	125
VI [Fe(CO)$_2$(PPh$_3$)$_2$(NNAr)]$^+$	1715-1725	H$_2$/Pd, 1 atm, 25°C prolonged	N=N not reduced	126
VII [RuX$_3$(PPh$_3$)$_2$(NNAr)] X = Cl,Br	1881-1895	Mild[j]	N=N not reduced	140
VIII [OsBr$_3$(PPh$_3$)$_2$(NNC$_6$H$_4$p-Me)]	1855	Mild[j]	N=N not reduced	140
IX [Ir(CO)Cl(PPh$_3$)$_2$(NNC$_6$H$_3$p-Br)] 6	1450	H$_2$/Pd, 1 atm, 25°C	Hydrazine complex	This work
X [PtCl(PEt$_3$)$_2$(NH=NAr)]$^+$	<1460[i]	H$_2$/Pt 1 atm, 25°C	Hydrazine complex[a]	4,5, 6,7
XI [IrH$_2$(PPh$_3$)$_2$(NH=NAr)]$^+$	1500-1520	H$_2$,1-3 atm 50-80°C	N=N not reduced	90, 92
XII [RhCl$_3$(PPh$_3$)$_2$(NH=NAr)]	1500-1530	H$_2$,1 atm 60°C	[RhCl$_3$(NH$_2$NHAr)- (PPh$_3$)$_2$]$_2$	108
XIII [Ir(CO)Cl(PPh$_3$)$_2$(NH=NAr)]$^+$ 5	1410-1442	H$_2$/Pd 1 atm,25°C	Hydrazine complex	This work

(a) Prolonged hydrogenation afforded NH_3, $ArNH_2$ (via $ArNHNH_2$) and $[PtHCl(PEt_3)_2]$.

(b) No details reported[125]: only that conditions of hydrogenation were mild and similar to those for $[PtCl(PEt_3)_2(N=NAr)]$

(c) Formulation as a bis-azo-complex has not been verified; it may equally well be a tetrazene complex[36,37].

(d) ν_{NN} not conclusively assigned.

(e) Postulated formulation on basis of i.r. data.

(f) pz = 1-pyrazolyl

(g) For assignment of ν_{NN}, see reference 127.

(h) Conditions not detailed, but more severe than for the hydrogenation of $[PtCl(PEt_3)_2(N=NAr)]$ and $[(Cp)Mo(CO)_2(N=NAr)]$

(i) ν_{NN} not available, but most likely lower than for $[PtCl(PEt_3)_2(N=NAr)]$ ($\nu_{NN} = 1440-1463$ cm^{-1}).

(j) No further details available.

A comparison of these results reveals no obvious correlation between the N=N stretching frequencies of the complexes and their ability to undergo hydrogenation; it can only be said that those complexes (V-VIII, XI in Table V-1) resistant to hydrogenation tend to have values for ν_{NN} lying towards the upper region of the range (1410-1895 cm^{-1}). Ibers *et al.*[134], in an attempt to diminish the region of overlap of the $\nu_{N=N}$ values for arylazo complexes having different bonding modes (1a, 1b and 2), postulated a set of empirical rules to bring

$$R-\overset{+}{N}\equiv N \rightarrow M \qquad \overset{\overset{+}{N}=N=M}{\underset{R}{\big|}} \qquad \overset{N=\bar{N}\overset{M}{\nearrow}}{\underset{R}{\big|}}$$
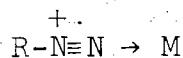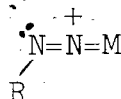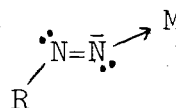
$$\text{1a} \qquad\qquad\qquad \text{1b} \qquad\qquad\qquad \text{2}$$

the various N=N stretching frequencies to a common scale: (1) subtract 50 cm^{-1} for first-row metals and 30 cm^{-1} for second-row metals; (2) subtract 80 cm^{-1} for singly charged and 140 cm^{-1} for doubly charged cationic complexes; (3) add 40 or 70 cm^{-1} for complexes with three or four tertiary phosphines, respectively. The complexes in Table V-1 can be considered to consist of five distinct types, viz:

(i)   arylazo complexes having phosphine ligands (I, III, IV, VI, VII, VIII)

(ii) arylazo complexes not having phosphine ligands (II, V)

(iii) an *ortho*-metalated arylazo complex in which the azo

function (-N=N-) is contained in a five-membered ring (IX)

(iv) aryldiimide complexes (X, XI, XII)

(v) an _ortho_-metalated aryldiimide complex in which the azo
function (-N=N-) is contained in a five-membered ring
(XIII).

No correlations can be drawn between ν_{NN} and ease of
hydrogenation for types (ii) - (v). Ibers' rules can be
applied only to type (i), and the results of so doing are de-
picted in Table V-2 in which ν_{NN} is the observed value and
ν'_{NN} the modified value. On application of his rules to cer-
tain phosphine-containing arylazo complexes, Ibers[134] classified
the PhN$_2$ complexes concerned into three distinct groups: (A)
those with values of ν'_{NN} lower than 1540-1560 cm^{-1} corresponding
to the doubly bent geometry (2); (B) those with values between
1540-1560 and 1700-1740 cm^{-1} corresponding to the singly bent
geometry (1b); (C) those with values greater than 1700-1740
cm^{-1} corresponding to the singly bent geometry, but tending
toward the totally linear case (1a). From Table V-2 it can be
seen that the complexes (I, III and IV) which were successfully
hydrogenated have ν'_{NN} ranging from 1440 to 1551 cm^{-1} and can be
classified as having doubly bent geometry. The complex (VI)
which resisted hydrogenation has a ν'_{NN} value of 1593 cm^{-1} and
a singly bent geometry, and the complexes VII and VIII, also
resistant to hydrogenation, have ν'_{NN} values of 1851 and 1855
cm^{-1}, respectively, indicative of a geometry tending toward

Table V-2

Observed (ν_{NN}) and Modified (ν'_{NN})
Stretching Frequencies for the Arylazo Complexes
I, III, IV and VI from Table V-1

Compound	ν_{NN}	ν'_{NN}	Whether hydrogenated
I [PtCl(PEt$_3$)$_2$(NNPh)]	1440	1440	Yes
III [Pt(PPh$_3$)$_2$(NNSO$_2$Ph)]	1450	1450	Yes
IV [RhCl$_2$(PPh$_3$)$_2$(NNPh)]	1614 & 1549	1551[a]	Yes
VI [Fe(CO)$_2$(PPh$_3$)$_2$(NNPh)]BF$_4$	1723	1593	No
VII [RuCl$_3$(PPh$_3$)$_2$(NNPh)]	1881	1851	No
VIII [OsBr$_3$)$_2$(NNC$_6$H$_4$p-Me)]	1855	1855	No

(a) The average of the two observed frequencies was taken in computing this value.

totally linear. Of course, until data on a much larger series

of arylazo complexes are available, no firm deductions can be

drawn. At best, it can be tentatively inferred that for those

complexes having relatively high N=N stretching frequencies

more powerful reducing agents are required (as described, for

example, in papers by Van Tamelen[135-138], wherein he resorts

to sodium naphthalide as the reducing agent for dinitrogen

complexes). Thus, the complex $[Fe(CO)_2(PPh_3)_2(NNC_6H_4 \underline{p}-Br)]BF_4$

$(\nu_{NN} = 1721 \text{ cm}^{-1})$, although resistant to hydrogenation under

mild conditions, reacted with sodium borohydride to give

several products, one of which exhibited mass spectral peaks

due to the ion $[\underline{p}-BrC_6H_4NHNH_2-BH_3]^{+139}$.

In view of the relevance of the ortho-metalated aryldi-

imide complexes, $\underset{\sim}{5}$, the ortho-metalated arylazo complexes, $\underset{\sim}{6}$,

and the aryltetrazene complexes, $\underset{\sim}{4}$, as models for the enzyma-

tic fixation of dinitrogen (c.f., Chapter I and the discussions

in Chapters II and III), it was considered of interest to

investigate their behaviour towards mild hydrogenation, as

reported below.

B. Hydrogenation of Some ortho-Metalated

Aryldiimide Complexes $[Ir(CO)Cl(PPh_3)_2(NH=NC_6H_3R)]BF_4, \underset{\sim}{5}$

Hydrogenation of the complexes $\underset{\sim}{5}e$ (R = $\underline{p}$-Br), $\underset{\sim}{5}j$

(R = $\underline{o}$-Br), $\underset{\sim}{5}n$ (R = $\underline{m}$-Br), $\underset{\sim}{5}i$ (R = $\underline{o}$-Cl) and $\underset{\sim}{5}k$ (R = $\underline{o}$-NO_2$) by

Table V-3

Elemental Analysis and Infrared Absorptions

(ν_{CO} and ν_{NH}) for the Arylhydrazine

Complexes $[Ir(CO)Cl(PPh_3)_2(NH_2NHC_6H_3R)]BF_4$,

7a-e.

Compound		Percentage Composition						Position of Absorption[a]	
No	R	Found			Calculated			ν_{CO}	ν_{NH}
		C	H	N	C	H	N	(cm^{-1})	(cm^{-1})
7a	p-Br	48.4	3.4	2.65	48.9	3.4	2.65	2048 (2046)[b]	3170,3230 3250,3310
7b	o-Br							2054	3174,3239 3256,3330
7c	m-Br							2056	3150,3180 3200,3270 3320
7d	o-Cl							2052	3174,3240 3256,3330
7e	o-NH₂	51.2	3.6	3.5	52.1 (50.7	3.8 3.5	4.2 4.1)[c]	2050	3180,3230 3290,3380 3410

a   All spectra as KBr pellet, except where noted.

b   Nujol mull

c   Calculated for R = NO₂

reacting ethanol solutions of the complexes for two hours with
H_2 at 1 atm. pressure and 25-30°C in the presence of a Pd
catalyst[a] afforded the related arylhydrazine complexes
$[Ir(CO)Cl(PPh_3)_2(NH_2NHC_6H_3R)]BF_4$, 7a (R = p-Br), 7b (R = o-Br),
7c (R = m-Br), 7d (R = o-Cl) and 7e (R = o-NH_2). The complexes,
7a-e, are listed in Table V-3, together with their main i.r.
absorptions and the elemental analyses for two of them (7a and
7e).

Apart from 7e (R = o-NH_2), which is a dull, brownish-
purple colour, the arylhydrazine complexes are pale-yellow
solids, soluble in ethanol and chloroform and insoluble in
diethyl ether.

Evidence for ortho-metalation in these complexes (7a-e)
was provided by the infrared aromatic substitution patterns due
to the C-H bending modes in the 750 to 900 cm^{-1} region; these
vibrations are present in the parent ortho-metalated aryldi-
imide complexes, 5e,i,j,k,n, (c.f. Chapter III-D2 and Table
III-4), and are retained in the related arylhydrazine complexes.
The infrared spectra (Diagram V-1) confirmed the presence of
the BF_4^- anion (strong, broad band centred at $\sim$ 1060 cm^{-1}) and
coordinated triphenylphosphine (C-H bending modes at $\sim$ 700 and
750 cm^{-1}). The infrared N=N stretching frequency at 1410 cm^{-1}
in the parent aryldiimide complex 5e (R = p-Br) was not

_____

(a) Hydrogenation did not occur in the absence of catalyst.

Wavenumber, cm^{-1}

Absorbance
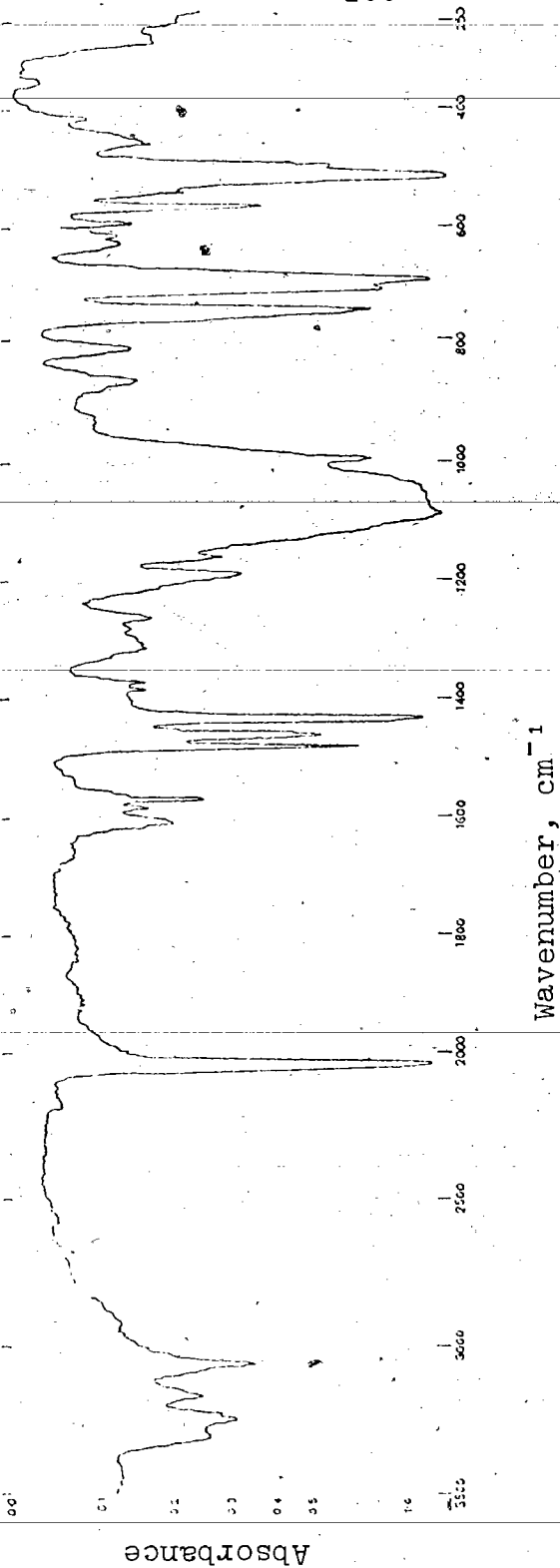
Diagram V-1. Infrared spectrum of $[Ir(CO)Cl(PPh_3)_2(H_2NNHC_6H_3\underline{p}\text{-Br})]BF_4$, $\underline{7a}$

observed in the arylhydrazine complex 7a (R = p-Br), consistent
with reduction of the diimide group to the hydrazine. All of
the complexes, 7a-e, exhibited a band in the 1610-1620 cm^{-1}
region assignable as an N-H bending vibration. The spectrum of
the arylhydrazine complex 7e, obtained by the reduction of the
ortho-nitrophenyldiimide complex, 5k, showed no bands charac-
teristic of the -NO$_2$ group, but did have two bands at 3380 and
3410 cm^{-1} (Table V-3) attributable to N-H stretching vibrations
of an -NH$_2$ group other than arylhydrazine; thus, it is consi-
dered that, in addition to reduction of the diimide function,
the nitro-group has also been reduced to the primary amine.

Further reaction of the p-bromophenylhydrazine complex,
7a, with hydrogen in the presence of a Pd catalyst at 60 psi
and 30°C for 30 hours failed to achieve hydrogenolysis, the
starting hydrazine complex being recovered unchanged.

C. Hydrogenation of the ortho-Metalated Arylazo
   Complex [Ir(CO)Cl(PPh$_3$)$_2$(N=NC$_6$H$_3$p-Br)], 6.

Reaction of a suspension of the pink complex 6 in ethanol with
hydrogen (1 atmosphere) in the presence of a palladium catalyst
at 25°C for two hours resulted in the formation of a red solu-
tion from which a deep, pink-red solid was isolated and recrys-
tallised from diethyl ether. On the basis of its elemental
analysis and infrared absorption data the compound was formula-
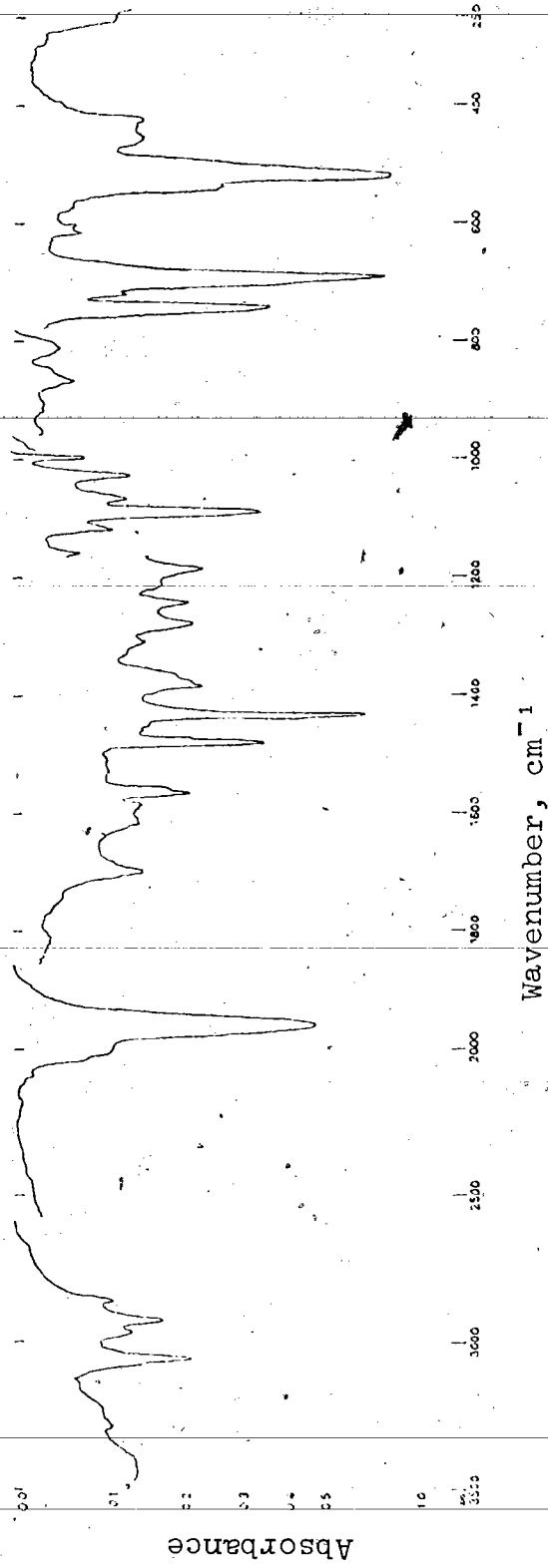
Diagram V-2. Infrared spectrum of $[Ir(CO)Cl(PPh_3)_2(H_2NNHC_6H_3\underline{p}-Br)]\cdot(C_2H_5)_2O$, 2.

ted as the molecular ortho-metalated para-bromophenylhydrazine complex [Ir(CO)Cl(PPh₃)₂(NH₂NHC₆H₃p-Br)]·(C₂H₅)₂O, 9, (Required: C, 54.31%; H, 4.43%; N, 2.69%. Found: C, 56.15%; H, 4.57%; N, 2.67%). The complex, 9, is soluble in ethanol and acetone and has some solubility in diethyl ether, from which it can be recrystallised. The infrared spectrum (Diagram V-2) exhibited characteristic bands at 3225 and 3285 cm⁻¹ (ν_{NH}); 1960 cm⁻¹ (ν_{CO}); 1620 cm⁻¹ (δ_{NH}); 810 and 865 cm⁻¹ (C-H bending modes of the 1,2,4-substituted phenyl ring) and 693 and 742 cm⁻¹ (C-H bending modes of the mono-substituted phenyl rings). The band assignable to ν_{NN} at 1450 cm⁻¹ in the spectrum of the parent para-bromophenylazo complex, 6, was absent from the spectrum of 9, whereas bands at 2860, 2925 and 2965 cm⁻¹ due to ν_{C-H} of diethyl ether were observed for 9 while absent from 6.

D. Hydrogenation of the Aryltetrazene Complex
[Ir(CO)(PPh₃)₂{N₄(C₆H₄p-Br)₂}]BF₄, 4d.

Both non-catalytic and catalytic hydrogenations of the aryltetrazene complex 4d were attempted under mild conditions. In the non-catalytic experiment, an ethanol solution of the red tetrazene complex was allowed to react with hydrogen at one atmosphere pressure and 28°C for three hours. No reaction took place, the starting complex being recovered.

In the catalytic hydrogenation of 4d, reaction did occur, but the result was inconclusive. The hydrogenation was performed as above, but

Table V-4

Infrared Spectroscopic Data for the Material
Resulting from Hydrogenation of
$[Ir(CO)(PPh_3)_2\{N_4(C_6H_4\underline{p}-Br)_2\}]BF_4$, $\underset{\sim}{4}$d.

Wave number (cm^{-1})$^{(a)}$	Assignment
3200-3300 (b)	N-H stretching
3060 (w-m)	Aromatic C-H stretching
2110 (w)	Ir-H stretching
2040 (w-m)	Ir-H stretching ⎫ Tentative
2000 (m)	carbonyl stretching
1050-1650 (b)	N-H bending deformation
1050-1100 (s,b)	BF$_4^-$ stretching
830 (m,b)	Aromatic C-H bending deformation of a para-substituted ring.
693 (s), 745 (m-s)	Aromatic C-H bending deformation of a mono-substituted ring.

a   KBr disc.

in the presence of a palladium catalyst. Evaporation of the
resulting pale-brown solution to small volume, followed by the
addition of diethyl ether afforded a pale-brown solid, (A).
The residue obtained by evaporation of the mother-liquor from
(A) was dissolved in diethyl ether and cooled to -14°C to
yield a second pale-brown solid, (B). Evaporation of the
mother-liquor from (B) gave a third pale-brown slightly tarry
solid, (C). Each of the products, (A), (B) and (C), gave
identical, rather weak infrared spectra exhibiting somewhat
broadened bands, indicative of impurity. The
main bands observed are listed in Table V-4 along with their
probable assignments. High resolution mass-spectral analysis
of the products (A), (B) and (C) confirmed the presence of
both carbon monoxide and nitrogen.

Although no apparently pure compound was isolated from
the hydrogenation reaction, it could be inferred from the infra-
red bands at 2000, 2040 and 2110 (ν_{CO} and ν_{Ir-H}), 1050-1100
(ν_{BF_4}-) and 693 and 745 cm^{-1} (δ_{C-H} due to PPh$_3$), and from the
mass spectral evidence for carbon monoxide, that a cationic
carbonyl bis-hydrido species was formed. The presence of bands
characteristic of N-H (3220-3250 cm^{-1}) and a para-substituted
ring (830 cm^{-1}) could be indicative of free organic moieties
such as para-bromoaniline or para-bromohydrazine. This
evidence would be consistent with cleavage of the iridium-
nitrogen bonds of 4d with possible formation of

para-bromoaniline. Thus, Beck et al.[37] found that catalytic

(Pd) hydrogenation of a complex formulated as $[(PPh_3)_2Pt(N_2SO_2Ph)_2]$,

and considered to be a tetrazene complex, gave $PhSO_2NH_2$ and a

material showing two weak absorptions at 2210 and 2160 cm^{-1},

suggesting the presence of the (thermally unstable) bis-hydride

complex, $[Pt(PPh_3)_2H_2]$ For the iridium tetrazene complex 4d,

then, it can be tentatively proposed that catalytic hydrogena-

tion results in formation of $[Ir(CO)H_2(PPh_3)_2]BF_4$ (10) and

para-bromoaniline, thus:

$$[Ir(CO)(PPh_3)_2\{N_4(C_6H_4\underline{p}-Br)_2\}]BF_4 \xrightarrow[\text{Pd, EtOH}]{H_2(1 \text{ atm})}$$

$$4d$$

$$[Ir(CO)H_2(PPh_3)_2]BF_4 + 2\underline{p}-BrC_6H_4NH_2 + N_2$$

$$10$$

Although no data are available in the literature for 10,

the perchlorate analogue, $[Ir(CO)H_2(PPh_3)_2]ClO_4$, is known[180,181]

and exhibits bands in the infrared (nujol mull) at 2165, 2085 and

2050 cm^{-1}. It is well established[98] that the nature of the

counterion can have a marked effect on infrared spectra in the

solid state, affecting both the intensity and frequency of the

bands, a factor which should be considered when comparing

10 with its perchlorate analogue. Other cationic bis-hydrido

iridium complexes exhibiting carbonyl (ν_{CO}) and iridium-hydride (ν_{Ir-H}) infrared stretching frequencies are [Ir(CO)H$_2$(PPh$_3$)$_3$]X (X=F, Cl, Br and I)[141] with average values for ν_{Ir-H} at 2160 and 2170 cm^{-1} and the average value for ν_{CO} at 2005 cm^{-1}; [Ir(CO)$_2$H$_2$(PPh$_3$)$_2$]PF$_6$[142] with ν_{Ir-H} at 2180 cm^{-1} and 2155 cm^{-1} and ν_{CO} at 2085 and 2050 cm^{-1}.

CHAPTER VI

Molecular Six-Coordinate Arylazo Complexes

A. Introduction

With a view to obtaining the elusive five-coordinate cationic arylazo complexes $[Ir(CO)Cl(PPh_3)_2(N_2Ar)]^+$ 2, it was considered that syntheses of the molecular six-coordinate arylazo complexes $[Ir(CO)Cl_2(PPh_3)_2(N_2Ar)]$ 8 followed by removal of the chloride ligand as AgCl might provide a feasible route. This chapter describes the synthesis, structure and properties of several six-coordinate complexes of this type, concluding with a discussion of the chloride abstraction which, unfortunately did not provide the desired five-coordinate complexes.

In 1969, Deeming and Shaw[144] had reported the successful synthesis of the analogous dimethylphenylphosphine complex $[Ir(CO)Cl_2(PMe_2Ph)_2(N_2Ph)]$ by reacting $[Ir(CO)Cl(PMe_2Ph)_2]$, PhN_2BF_4 and LiCl in a methanol-water medium. Attempts (in this work) to prepare 8 from Vaska's complex, 1, by the method of Deeming and Shaw were unsuccessful, resulting only in a high recovery of 1 and a low yield of an incompletely characterised product 12 analysing for one nitrogen atom per iridium atom. The desired arylazo complexes 8 were obtained in high yield, however, when the methanol-water

medium was replaced by neat acetone.

Concurrent with this work on the complexes 8, Ibers and Haymore[119] reported the isolation and characterisation of a series of these complexes (Ar = C_6H_5; p-FC_6H_4; p-$CH_3C_6H_4$) by a similar reaction, but made no mention of the solvent system employed. It appears, though, that the course of the reaction is quite solvent dependent: with acetone, a high yield of 8 plus a low yield of 12 resulted, whereas with benzene-ethanol (or isopropanol) a high yield of 12 and none of the arylazo complex, 8, was obtained. Also, as mentioned earlier, with methanol-water, a low yield of 12 and, again, none of the desired complex, 8, resulted.

The currently known molecular six-coordinate arylazo complexes, as reported in the literature, are listed in Table VI-1 which contains one other example of the use of lithium halide in the synthesis, namely [$MX_3(PPh_3)_2(N_2Ar)$] (M = Ru; Os; X = Cl, Br) from [$MX_2(PPh_3)_2$], ArN_2BF_4 and LiX in acetone medium[108,140].

B. Synthesis

The arylazo complexes [$Ir(CO)Cl_2(PPh_3)_2N_2Ar$], 8 a-f (see Table VI-2), were readily prepared by addition of the requisite aryldiazonium tetrafluoroborate and lithium chloride to a suspension of [$Ir(CO)Cl(PPh_3)_2$] 1 in acetone; the molar ratio of 1, ArN_2BF_4 and LiCl was held at 1:1:1. In most cases,

Table VI-1

Molecular Six-Coordinate Transition Metal
Arylazo Complexes

Complex	ν_{NN} (cm^{-1})	References
I $[Ir(CO)Cl_2(PMe_2Ph)_2(N_2Ph)]$	(a)	144
II $[MX_3(PPh_3)_2(N_2Ar)]^{(b)}$	1858-1895	108,140,148
III $[Ir(CO)Cl_2(PPh_3)_2(N_2Ph)]$	1464	119,134
IV. $[ReCl_2(PMe_2Ph)_3(N_2Ph)]$	(a)	145
V $[ReCl_2(NH_3)(PMe_2Ph)_2(N_2Ph)]$	1534	146,147
VI $[RB(pz)_3M(CO)_2(N_2Ar)]^{(c)}$	1530-1580	125,127
VII $[HB(pz)_3Mo(NO)Cl(N_2Ph)]$	1642	149

(a) ν_{NN} value not reported.

(b) M = Ru, Os; X = Cl, Br; Ar = C_6H_5, p-C_6H_4Me, p-C_6H_4OMe,

p-C_6H_4Cl, p-$C_6H_4NO_2$

(c) R = H, pz; M = Mo, W; pz = 1-pyrazolyl; Ar = C_6H_5, p-C_6H_4F,

m-C_6H_4F, p-$C_6H_4NO_2$, o-$C_6H_4CH_3$, o,o -$C_6H_3(CH_3)_2$

Table VI-2

Elemental Analyses, Colour and Yields for
the Six-coordinate Molecular Arylazo Complexes
$[Ir(CO)Cl_2(PPh_3)_2(N_2C_6H_4R)]$, 8 a-f

Compound	R	Percentage Composition						Colour	Yield (%)
		Found			Calculated				
		C	H	N	C	H	N		
$8a$(a)	H	56.70	4.26	2.71	$\lbrace$56.41 (56.07	4.23 3.84	2.86 3.04$)$b	Orange	70
$8b$(a)	p-F	55.40	4.06	2.73	55.43 (54.99	4.04 3.66	2.81 2.99$)$b	Yellow-orange	65
$8c$	p-Br	50.58	3.57	2.49	51.64	3.45	2.80	Orange	50
$8d$	p-OCH$_3$	54.16	3.94	2.26	55.50	3.93	2.94	Yellow	20
$8e$	o-F	54.85	3.76	2.60	54.99	3.66	2.99	Orange	50
$8f$	m-NO$_2$	53.31	3.53	4.36	53.39	3.55	4.35	Orange	90

(a) Formulated with 1 mole $(CH_3)_2CO$ per 1 mole of complex.

(b) Calculated values for formulation without $(CH_3)_2CO$.

the product precipitated readily from solution at room tempera-
ture. Where necessary, the reaction solution was cooled to
+3°C to induce precipitation of the arylazo complex, but caution
was required as further cooling may also cause precipitation of
lithium tetrafluoroborate and a solid(12) having a low nitrogen
content. In addition to the complexes listed in Table VI-2,
the synthesis of the 2,6-difluorophenylazo complex was
attempted. However, the reaction of 1, 2,6-difluorophenyl-
diazonium tetrafluoroborate and lithium chloride in
acetone medium afforded only the "low-nitrogen" product 12.

C. Properties

1. General Properties

The arylazo complexes 8a-f are yellow to orange crystal-
line solids. They are quite stable over prolonged periods to
air, but appear to be somewhat light-sensitive. The complexes
are readily soluble in benzene, dichloromethane and chloroform,
only slightly soluble in acetone, ethanol, acetonitrile and
diethylether, and insoluble in water.

2. Infrared Spectroscopy and Some Structural Implications.

The main infrared absorption data are presented in
Table VI-3 and a typical spectrum, that of 8b, is shown in
Diagram VI-1. In addition to the absorptions listed in

Table VI-3

Some Infrared Spectral Data for the Arylazo
Complexes $[Ir(CO)Cl_2(PPh_3)_2(N_2C_6H_4R)]$, 8 a-f

Compound	R	ν_{CO} (b)	Position of Absorption (cm^{-1}) (a)		
			ν_{NN} (b)	δ_{CH}	Other Bands
				(Arylazo ring)	
8a	H	2058	1470 1464 (c)	(d)	
8b	p-F	2055	1470	840	1220 (ν_{CF})
8c	p-Br	2050	1465	830	
8d	p-OCH₃	2050	1455	835	1030 $(\nu_{COC},$ sym- metric) 1250 $(\nu_{COC},$ asym- metric) 2840 (ν_{CH_3})
8e	o-F	2060	1465 (e)	(d)	1220 (ν_{CF})
8f	m-NO₂	2050	1455	803 835	1353 $(\nu_{NO_2},$ symmetric) 1530 $(\nu_{NO_2},$ asymmetric

(a) KBr pellet

(b) ± 1 cm^{-1}; all other bands, ± 2 cm^{-1}

(c) Frequency when the iridium-bonded nitrogen is ^{15}N

(d) Probably obscured by ring C-H bending modes of the PPh₃ ligands.

(e) Occurred as a shoulder on a strong aromatic C=C absorption at 1485 cm^{-1}.
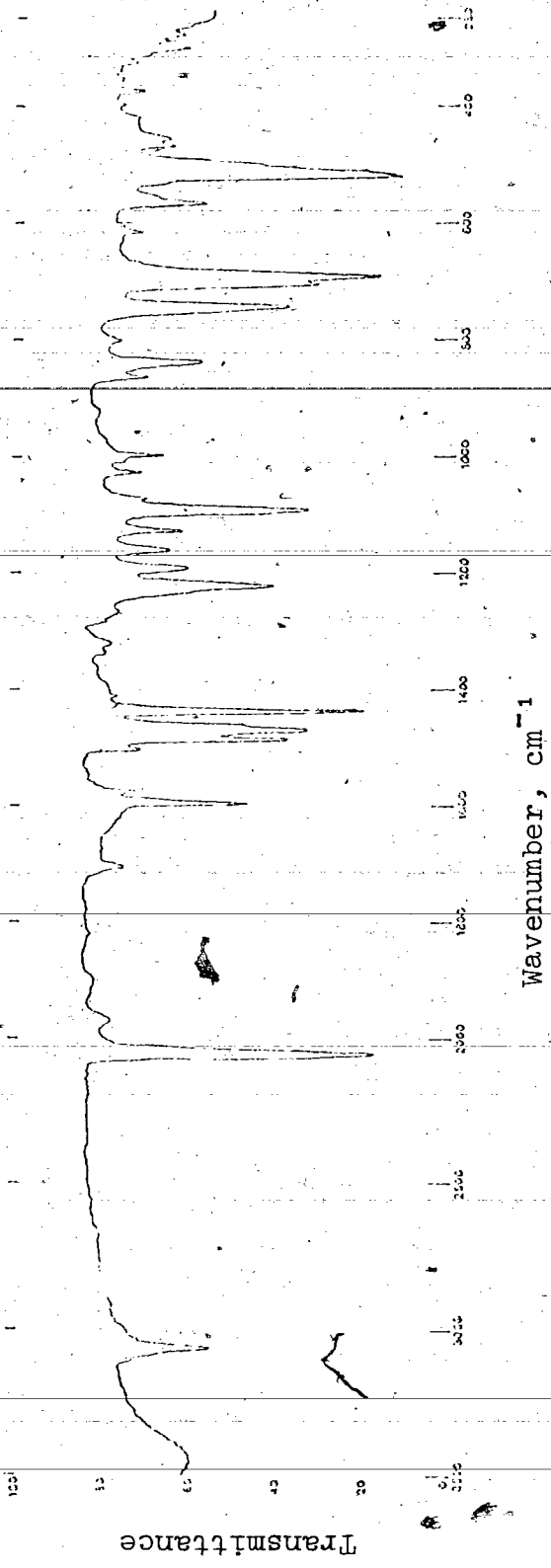
Diagram VI-1. Infrared spectrum of $[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4\underline{p}-F)] \cdot (CH_3)_2CO$, 8b

Table VI-3, the spectra of all the complexes 3a-f exhibited absorptions at ca. 700 and 750 cm^{-1} due to the ring C-H bending modes of the triphenylphosphine ligands.

Assignment of the absorption at 1470 cm^{-1} as ν_{NN} for the phenylazo complex 3a was confirmed by the observation of a shift in this frequency to 1464 cm^{-1} for the isotopically substituted analogue, [Ir(CO)Cl$_2$(PPh$_3$)$_2$(^{15}N=NC$_6$H$_5$)], synthesised from [C$_6$H$_5$N≡^{15}N] BF$_4$.

No obvious trend can be inferred between ν_{CO} and/or ν_{NN} and the electronic nature of the R substituents in the complexes 3a-f. However, the relatively low values for ν_{NN} in these complexes give some indication as to the mode of bonding between the arylazo function and the iridium metal. There are few structural determinations of arylazo complexes yet available; the pertinent data for those that have been reported[134,145,150,151] are listed in Table VI-4. Structural studies of metal nitrosyl complexes, though, are numerous and the isoelectronic nature of NO$^+$ and ArN$_2$$^+$ on the one hand and NO$^-$ and ArN$_2$$^-$ on the other hand allows useful structural comparisons to be made between the arylazo and the nitrosyl complexes. It has been clearly demonstrated that nitric oxide can coordinate formally either as NO$^-$ (linear M-N-O) or NO$^-$ (bent M-N-O, 120°), a recent tabulation[152] having eight nitrosyl complexes out of 52 in which the M-N-O angle is between 120 and 128°. By analogy, then, the coordinated aryldiazonium cation may also be expected

Table VI-4

Some Structural Data and Observed (ν_{NN}) and
Modified (ν'_{NN})[a] Stretching Frequencies
for Transition Metal Arylazo Complexes

| Compound | Angle, deg. | | Distance, Å | | ν_{NN} ν'_{NN} | Ref |
	M-N-N	N-N-Ar	M-N	N-N	$(cm^{-1})(cm^{-1})$	
I [ReCl$_2$(PMe$_2$Ph)$_3$(N$_2$Ph)]	172	118	1.80	1.23	(b)	145
II [RuCl$_3$(PPh$_3$)$_2$(N$_2$Ar)][c]	171.2(9)	135.90(11)	1.796(9)	1.144(10)	1882 1852 (Ar=C$_6$H$_5$)	150
III [HB(pz)$_3$Mo(CO)$_2$(N$_2$Ph)]	174.21(12)	121.09(21)	1.825(4)	1.211(6)	1559	151
IV [RhClL(N$_2$Ph)]PF$_6$[d]	125(1)	119(1)	1.954(8)	1.17(2)	1627 1557 1561 1491	134

(a) See Chapter V.A, Chapter VI.C2 and reference 134

(b) No value reported

(c) Ar = C$_6$H$_4$p-CH$_3$

(d) L = PhP((CH$_2$)$_3$PPh$_2$)$_2$

to exhibit bent or linear M-N-N moieties, as already indicated in Chapter V.A and as outlined in the possible bonding schemes, 1a, 1b and 2 below:

$$\overset{..}{M} \quad :N\equiv\overset{+}{N}\text{-Ar} \quad \longrightarrow \quad \overset{..}{M} \leftarrow N\equiv\overset{+}{N}\text{-Ar}$$

$$1 \qquad\qquad\qquad 1a$$

$$\overset{2+}{M} \leftarrow \overset{\bar{..}}{N} \underset{\underset{..}{N}\text{-Ar}}{\Big\Vert} \quad \longleftrightarrow \quad \overset{+}{M} \rightleftharpoons N=\overset{..}{N} \diagdown_{Ar}$$

$$2 \qquad\qquad\qquad\qquad 1b$$
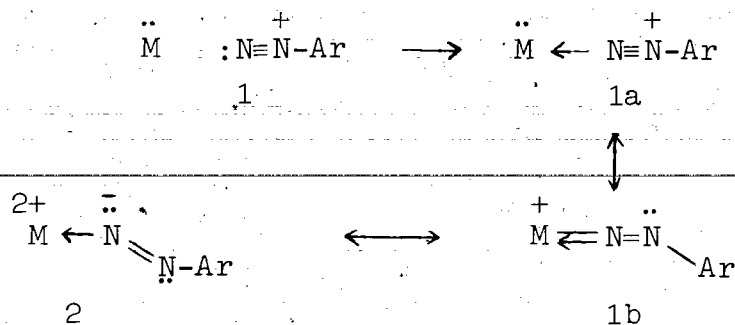
In 1, ArN_2^+ is behaving as a Lewis base and a π-acceptor, resulting in a linear M-N-N unit and either a linear (1a) or a bent (1b) N_2^+-Ar unit, whereas in 2 it is acting as a Lewis acid resulting in a doubly bent $M \leftarrow N_2^{2+} - Ar^-$ unit. In the ruthenium complex II, Table VI-4, the N-N bond length of 1.144Å lies between a nitrogen-nitrogen double and triple bond, indicative of a geometry lying somewhere between 1a and 1b; the N-N-Ar bond angle of 135.9° favours the singly bent geometry, 1b. The N-N stretching frequencies for a series of complexes of this type, $[MX_3(PPh_3)_2(N_2Ar)]$ (M = Ru, Os; X = Cl, Br)[140], lie in the range 1850-1890 cm^{-1}, which can thus be considered as indicative of a bond order for N-N of greater than two and less than three. The molybdenum complex III, Table VI-4, has an N-N stretching frequency of 1559 cm^{-1} and the crystallographic data verifies the singly bent geometry, 1b. Thus, for the

rhenium complex I, Table VI-4, which has structural parameters very similar to the complex III, one could predict a ν_{NN} value in the region of 1560 cm^{-1}. The rhodium complex IV, Table VI-4, affords the only structural example of an arylazo analogue of NO$^-$ in which the M-N-N-Âr unit is doubly bent (2). This complex exhibits two infrared bands at 1627 and 1561 cm^{-1} associated with the -N=N- linkage. Recently, compounds formulated as [Ru(bipy)$_2$Cl(N$_2$C$_6$H$_4$R)][PF$_6$]$_2$ (X = p-OCH$_3$, p-CH$_3$) have been reported[153] with ν_{NN} values of 2095 (p-OCH$_3$) and 2080 cm^{-1} (p-CH$_3$). Such high N-N stretching frequencies suggest that they have a geometry tending towards the totally linear case, 1a, and their chemistry[153] lends support to this formulation.

It seems, then, on the basis of the foregoing structural data for arylazo complexes and the obvious amphoteric nature of the arylazo ligand, analogous to that of the nitrosyl ligand, that high N-N stretching frequencies (greater than approx. 1600 cm^{-1}) are indicative of the singly bent geometry (1b), tending towards the totally linear case (1a) as ν_{NN} increases, whereas the lower N-N stretching frequencies infer the doubly bent geometry (2). Thus, the six-coordinate iridium complexes [Ir(CO)Cl$_2$(PPh$_3$)$_2$(N$_2$Ar)], 8a-f, having N-N stretching frequencies lying in the range 1455 to 1470 cm^{-1} are expected to have the geometry depicted in 2, possessing a bent Ar$\overline{N}_2$ grouping and conforming to the 18 electron formalism. As previously outlined in Chapter V.A, Ibers et al.[134] applied

an empirical set of rules to bring the ν_{NN} values of arylazo complexes to a common scale in an effort to reduce the region of overlap which obviously exists (c.f., complexes III and IV, Table VI-4). From the modified N-N frequencies (ν'_{NN}, Table VI-4) thus obtained it can be seen that the values for the iridium complexes 8a-f (ν'_{NN} = 1455 - 1470 cm^{-1}) lie well within the range of less than 1540 - 1560 cm^{-1} proposed by Ibers et al.[134] for the doubly bent geometry (2).

As discussed later in Section D, the molecular six-coordinate arylazo complexes, 8, can, in principle, be converted to the cationic five-coordinate species, 2, by removal of a chloride ligand as silver chloride:

$$[IrCl_2(CO)(PPh_3)_2(N_2Ar)] \xrightarrow{\frac{AgBF_4}{C_6H_6}} [Ir(CO)Cl(PPh_3)_2(N_2Ar)]BF_4 + AgCl$$

8 2
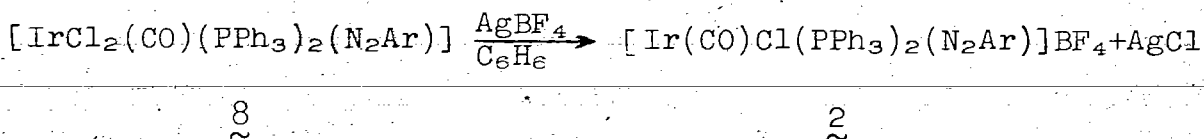
It is of considerable interest in relation to the mode of bonding of the aryldiazonium cation to the iridium that the five-coordinate complexes, 2, appear to readily break down in solution, since the only observed products were the aryldiazonium cation, ArN_2^+, and Vaska's complex, $[Ir(CO)Cl(PPh_3)_2]$;[a] this behaviour is not exhibited by the six-coordinate complexes, 8a-f. The ready loss of the arylazo ligand in this manner from the five-coordinate complexes suggests that it is bound to the iridium as ArN_2^+. Thus, removal of a chloride ligand from 8 has resulted in a change of the bonding mode of the arylazo

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a. See footnote b on page 124

ligand from ArN_2^- in the six-coordinate complex to ArN_2^+ in the five-coordinate case, providing further evidence for an ArN_2^- moiety in the six-coordinate complexes, 8a-f. An analogy to this type of behaviour is provided by the two cobalt nitrosyl complexes, trans-$[Co(NO)(NCS)(C_6H_4\{As(CH_3)_2\}_2)_2]^+$ and $[Co(NO)(C_6H_4\{As(CH_3)_2\}_2)_2]^{2+}$ which differ only by one pseudo-halide ligand. The bonding of the nitrosyl ligand in the six coordinate complex consists of $[Co(III)-(N=O^-)]^{2+}$ (angle Co-N-O = 135°), while the pentacoordinate trigonal bipyramidal complex is best formulated as $[Co(I)-(N\equiv O^+)]^{2+}$ (angle Co-N-O = 179°)[122].

D. Reactions

1. Reactions with Ag^+

Introduction

The six-coordinate arylazo complexes were reacted with Ag^+ (one equivalent) to effect the removal of one chloride ligand. The purpose behind this was two-fold: (a) to provide a route to the cationic five-coordinate arylazo complexes $[Ir(CO)Cl(PPh_3)_2(N_2Ar)]^+$, 2, previously, and unsuccessfully, attempted by reacting Vaska's complex $[Ir(CO)Cl(PPh_3)_2]$, 1, with aryldiazonium cations, ArN_2^+; (b) to leave a vacant coordination site on the metal where (on the assumption that the complexes 2 might be unstable with respect to ortho-metalation) ortho-metalation of either the arylazo ring or a

triphenylphosphine ring could occur, with concomittant protonation of the azo function. ortho-Metalation via the arylazo ring to give a five-membered metallocycle was considered to be more likely than via a triphenylphosphine ring to give the less stable four-membered metallocycle, e.g.:

$$[Ir(CO)Cl_2(PPh_3)_2(N_2Ph)] + Ag^+ \rightarrow [Ir(CO)Cl(PPh_3)_2(N_2Ph)]^+ + AgCl$$

8a   2

5a
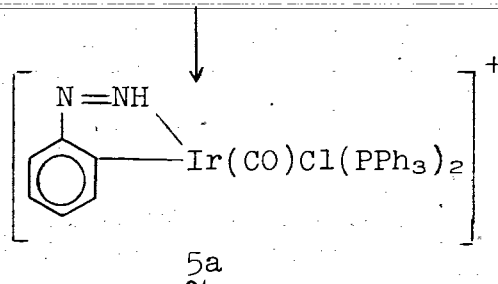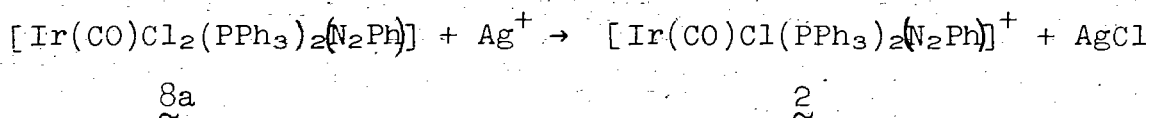
Results

The product obtained from the reaction between the six-coordinate phenylazo complex, 8a, and silver perchlorate (one equivalent) in benzene solution gave an infrared spectrum indicative of the perchlorato phenylazo complex $[Ir(CO)Cl(OClO_3)(PPh_3)_2(N_2Ph)]$ with bands at 2058 cm^{-1} (ν_{CO}) and 1470cm^{-1} (ν_{N_2}), and three bands at 1130,1112 and 638cm^{-1} assignable to vibrations of a monodentate perchlorato ligand (c.f., Chapter III.2). Although this complex was not further characterised, it seems that the only effect of the reaction of 8a with AgClO$_4$ was the replacement of a chloride ligand by a perchlorate ligand. However, the reactions with silver tetrafluoro-

Table VI-5

Reactions of the Six-coordinate Arylazo Complexes (8) with Silver Tetrafluoroborate

$$[Ir(CO)Cl_2(PPh_3)_2(N_2C_6H_5R)] + AgBF_4 + X \xrightarrow{\text{S}} \text{Products}$$

Compound	R	Solvent system (S)	Other Conditions (X)	Products[a]		
				Diazonium Salt	Vaska's Complex	Other
8b	p-F	C_6H_6		Yes	Yes	
8c	p-Br	C_6H_6		Yes	Yes	
8f	m-NO$_2$	C_6H_6		Yes	Yes	
8d	p-OCH$_3$	C_6H_6		Yes	Yes	
8e	o-F	C_6H_6	$(C_2H_5)_3N$	Yes	Yes[b]	$(C_2H_5)_3NH^+Cl^-$
8d	p-OCH$_3$	C_6H_6	$KOC(CH_3)_3$	Yes	Yes	
8d	p-OCH$_3$	$C_6H_6-CH_3NO_2$		No	No	
8c	p-Br	$C_6H_6-(CH_3)_2CO$		No	Yes[c]	
8b	p-F	$C_6H_6-C_2H_5OH$		No	No	Aryltetrazene
8c	p-Br	$C_6H_6-C_2H_5OH$		No	Yes[c]	Aryltetrazene + Aryldiimide
8e	o-F	$C_6H_6-C_2H_5OH$		No	No	Aryldiimide
8f	m-NO$_2$	$C_6H_6-C_2H_5OH$		No	Yes[c]	Aryldiimide

(a) AgCl was a product of all the listed reactions.

(b) The diazonium salt was isolated only on re-acidification $(C_2H_5)_3N$ forms an adduct with diazonium salts.

(c) Isolated only in small amount.

borate in place of silver perchlorate proved to be of much greater interest; they are discussed below, and are summarised in Table VI-5.

When the six-coordinate arylazo complexes $[Ir(CO)Cl_2(PPh_3)_2(N_2Ar)]$ were reacted with $AgBF_4$ in a 1:1 molar ratio in benzene solution the products of the reactions were Vaska's complex, $[Ir(CO)Cl(PPh_3)_2]$, 1, the aryldiazonium tetrafluoroborate, $ArN_2^+BF_4^-$, and silver chloride. As already inferred (c.f., p 119), it appears that the five-coordinate arylazo complex, 2, resulting from removal of a chloride ligand from 8, is an unstable entity in solution, readily releasing the arylazo ligand as the free diazonium cation, ArN_2^+. When the reaction of the six-coordinate complexes with $AgBF_4$ was carried out in benzene-ethanol medium, however, the products obtained were not Vaska's complex, ArN_2^+ and AgCl but were the five-coordinate aryltetrazene complex, 4, and/or the six-coordinate aryldiimide complex, 5, along with AgCl. Thus, in the presence of ethanol, the Vaska's complex, 1, and the aryldiazonium tetrafluoroborate formed by decomposition of the five-coordinate complex, 2, react as in the normal synthesis of the aryltetrazene (4) and aryldiimide (5) complexes. The overall reaction sequence is depicted below.

The results of these reactions of $AgBF_4$ with the complexes 8 have mechanistic implications, as will be discussed in detail in Chapter VII. It is sufficient at present to point out that

$[Ir(CO)Cl_2(PPh_3)_2(N_2Ar)]$ + AgBF$_4$

$\underset{\sim}{8}$

$\xrightarrow{C_6H_6}$ $[Ir(CO)Cl(PPh_3)_2(N_2Ar)]BF_4$ + AgCl

$\underset{\sim}{2}$

$\downarrow$

$[Ir(CO)Cl(PPh_3)_2]$ + ArN$_2^+$BF$_4^-$

$\underset{\sim}{1}$

$\downarrow C_6H_2OH$

$[Ir(CO)(PPh_3)_2(N_4Ar_2)]BF_4$ + $[Ir(CO)Cl(PPh_3)_2(HN_2Ar)]BF_4$

$\underset{\sim}{4}$ $\underset{\sim}{5}$
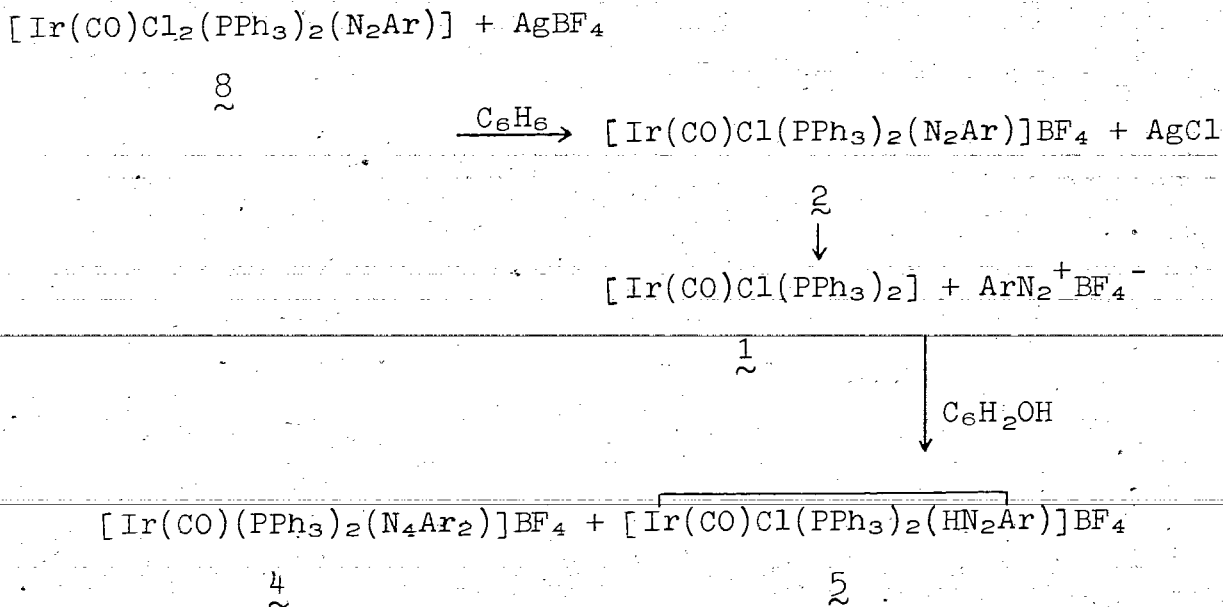
the cationic five-coordinate arylazo complex ($\underset{\sim}{2}$) appears to
be unstable, not to intramolecular ortho-metalation but,
rather, to a redox dissociation to form Vaska's complex
($\underset{\sim}{1}$) and the aryldiazonium salt.[b] Thus, any mechanism for the
formation of the aryldiimide complexes ($\underset{\sim}{5}$) which involves
intramolecular ortho-metalation of a cationic five-coordinate
arylazo intermediate ($\underset{\sim}{2}$) may well be invalidated.

A further attempt at inducing ortho-metalation by
removal of a chloride ligand from the six-coordinate complexes
($\underset{\sim}{8}$d,e), this time under basic conditions (to facilitate the
removal of an ortho-proton from the ring undergoing ortho-

b. The five-coordinate complex, $\underset{\sim}{2}$, has since been synthesised by
Dr. N. Farrell and its facile disproportionation to 1 and
ArN$_2$BF$_4$ in C$_6$H$_6$ solution has been demonstrated (c.f. Chapter
VII). Also, the reaction of $\underset{\sim}{2}$ with Cl$^-$ in acetone solution
at -25°C produced $\underset{\sim}{8}$.

metalation) was unsuccessful. Thus, reaction of 8d and 8e with AgBF$_4$ in benzene solution and in the presence of potassium t-butoxide and triethylamine,- respectively, again produced Vaska's complex (1), the aryldiazonium salt and silver chloride.

Finally, the formation of the aryltetrazene and aryl-diimide complexes (4 and 5, respectively) from the reaction between the six-coordinate complexes (8) and AgBF$_4$ in benzene-ethanol medium, and their non-formation in neat benzene-acetone or benzene-nitromethane media (Table VI-5) further substanti-ates the necessity for ethanol (or its equivalent) in the syntheses of both 4 and 5 (c.f., Chapter VII).

2. Reaction with HBF$_4$

In keeping with the postulated doubly bent nature of the arylazo ligand, ArN̄$_2$, in the complexes 8a-f (c.f., Chapter VI, C2), protonation of the azo (-N=N-) function by H$^+$ has been achieved. Thus, for example, treatment of a suspension of the yellow-orange complex [Ir(CO)Cl$_2$(PPh$_3$)$_2$(N=NC$_6$H$_4$p-F)], 8b, in diethyl ether with an excess of HBF$_4$ (48% in aqueous solution) afforded, in 80% yield, a pale-yellow solid formula-ted on the basis of infrared spectral data and elemental analysis as the p-fluorophenyldiimide complex [Ir(CO)Cl$_2$(PPh$_3$)$_2$(HN=NC$_6$H$_4$p-F)]BF$_4$, 11. The complex analysed as C:50.84%, H:3.38% and N:2.81%, requiring C:50.52%, H:3.10% and N:2.74%. The infrared spectrum of 11 (DiagramVI-2) exhi-bited a medium-intensity band at 3110 cm^{-1} and a broad, strong

Wavenumber, cm^{-1}

Transmittance
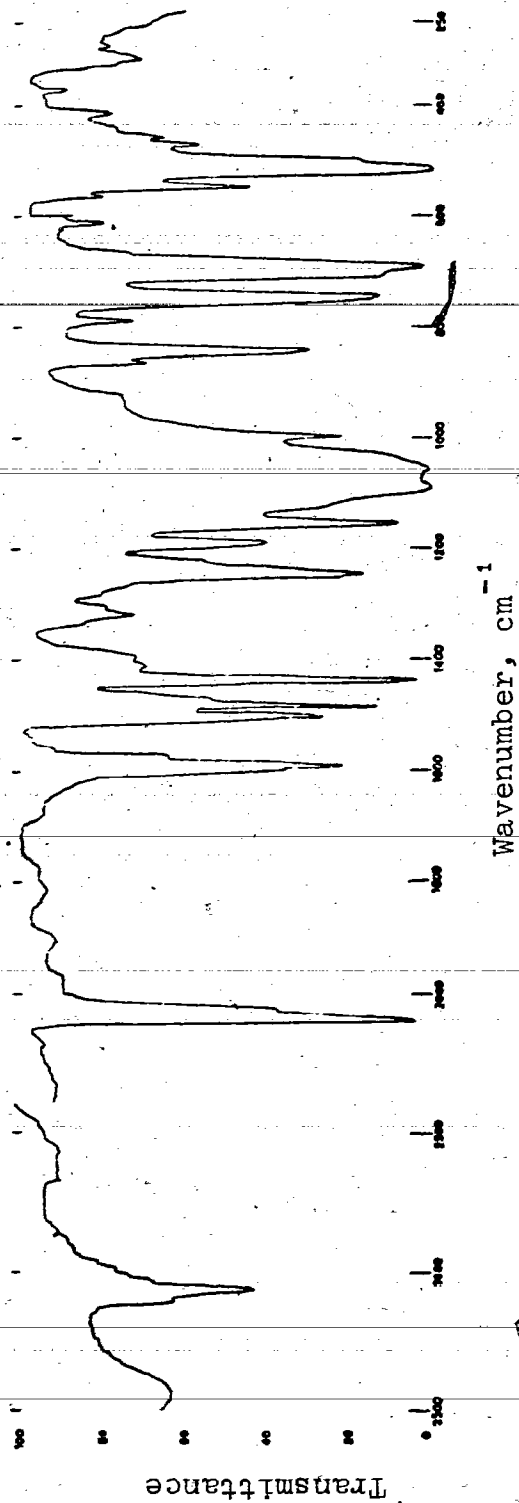
Diagram VI-2. Infrared spectrum of $[Ir(CO)Cl_2(PPh_3)_2(HN=NC_6H_4\underline{p}-F)]BF_4$, 11

absorption centred at ~1060 cm^{-1}, both of which were absent from the spectrum of 8b itself, and which were removed by treatment of 11 with base (resulting in the re-formation of 8b); the former band is attributed to ν_{N-H} and the latter to ν_{BF_4}-. The carbonyl stretching frequency shifted on protonation of 8b from 2055 cm^{-1} to 2090 cm^{-1} in 11, and the N=N stretching frequency observed at 1470 cm^{-1} in 8b was absent from the spectrum of 11.

The protonation of 8b was found to be reversible, a suspension of the diimide complex, 11, in diethyl ether being readily and quantitatively deprotonated on treatment with triethylamine:

$$[Ir(CO)Cl_2(PPh_3)_2(N=NC_6H_4\underline{p}\text{-}F)] \underset{Et_3N}{\overset{HBF_4}{\rightleftharpoons}} [Ir(CO)Cl_2(PPh_3)_2(HN=NC_6H_4\underline{p}\text{-}F)]BF_4$$

$$8b \qquad\qquad\qquad\qquad\qquad\qquad\qquad 11$$
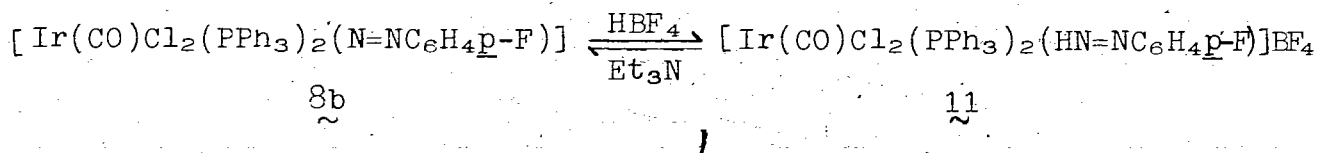
In fact, deprotonation was so facile that attempts to dissolve 11 in methanol, ethanol and acetonitrile resulted, in each case, in its reconversion to 8b. Thus, although the diimide complex 11 is quite stable in the solid state, it was found to be unstable in solution: in addition to its ready deprotonation in the solvents cited above, it was also found to be unstable in both acetone and chloroform, undergoing decomposition with the formation of some diazonium ion, $\underline{p}$-FC$_6$H$_4$N$_2$$^+$, as indicated by the appearance of an absorption at 2280 cm^{-1} (typical of ν_{N_2}+) in the infrared spectra of the material recovered after stirring 11 in either acetone or chloroform.

Only from solvents in which it was insoluble (e.g., diethyl
ether, benzene, water) could 11 be recovered unchanged, ren-
dering unsuccessful all attempts to obtain an nmr signal
characteristic of a single N-H proton.

CHAPTER VII

Mechanistic Studies and Discussion

A. Introduction

The fact that reaction between Vaska's complex, 1, and certain

aryldiazonium cations, ArN_2^+, should result in such unexpected

products as the aryltetrazene complexes, 4, (c.f. Chapter II)

and the ortho-metalated aryldiimide complexes, 5 (c.f. Chapter

III) raises an intriguing problem regarding the nature of the

mechanistic route to these compounds. All other reported

reactions of transition metal complexes with ArN_2^+ to give

nitrogen-containing complexes have provided either (a)

arylazo complexes[3,108,119,125-7,140,144-7,149] ($M-N_2Ar$),

involving direct coordination of ArN_2^+ to the metal, or (b)

non-ortho-metalated aryldiimide complexes[4-6,90,91]

($M-NH=NAr$), involving insertion of ArN_2^+ into a metal-hydride

bond. In the formation of 4 and 5, however, the possibilities

would seem to be (a) initial coordination of ArN_2^+ to iridium,

followed by further reaction on the arylazo ligand, or (b)

initial modification of ArN_2^+ (by reaction with an entity other

than the iridium of Vaska's complex), followed by coordination

of this modified species to iridium; these possibilities are

discussed in Section B.

Other features of interest are: (i) no other synthetic

routes to ortho-metalated aryldiimide complexes have been

reported;[a] (ii) the known aryldiimide complexes (non-ortho-metalated) have resulted either by insertion[4-6,90,91] of ArN_2^+ into a metal-hydride bond or by protonation[108-9,119,140] of the azo (-N=N-) function of an arylazo complex; (iii) all other instances of the syntheses of aryltetrazene complexes have involved reaction between an organic azide, ArN_3, and a transition metal complex.[30-33,36,37]

The most obvious feature of the reaction conditions leading to 4 and 5 when 1 is allowed to react with ArN_2^+ is the necessity for the presence of either ethanol or iso-propanol; the implications of this are discussed in Section C.

The formation of both an aryltetrazene complex and an ortho-metalated aryldiimide complex under the same reaction conditions requires that the participation of a common intermediate be considered. In this chapter, evidence, consistent with the currently available experimental data, is presented (Section C) for such an intermediate involved in possible pathways (Section E) to both 4 and 5; the possible nature of the intermediate is discussed in Section D.

Elucidation of the mechanistic routes has been greatly hindered by the failure, to date, to establish conditions eliminating competing reactions and leading to only one product, 4 or 5. Thus, (a) syntheses utilising the analogues, $[IrA(CO)(PPh_3)_2]$, of 1 where A represents an anionic ligand (F, Br, I, $OClO_3$) more labile than Cl were unsuccessful in increasing the yield of the aryltetrazene complex; (b) con-

_____

(a) A recent paper describes the synthesis of the ortho-metalated aryldiimide complex $[IrCl_2(PPh_3)_2(NH=NC_6H_4p-OCH_3)]$, from reaction between $[IrH_2(PPh_3)_3(NH=NC_6H_4p-OCH_3)]$ and chloroform at room temperature.[132]

ducting the synthesis in the presence of Ag^+ to facilitate removal of the chloride ligand was only partially successful in that, although the yield of the aryltetrazene complex was increased (Table VIII-1), that of the _ortho_-metalated diimide complex remained unaltered; (c) the use of aryldiazonium cations blocked in both _ortho_-positions to prevent formation of the _ortho_-metalated complexes, 5, also prevented tetrazene formation; (d) reactions in the presence of added Cl^- (to prohibit formation of the aryltetrazene complex by preventing loss of the chloride ligand) were completely unrewarding in that formation of both 4 and 5 was prevented.

B. Possible modes of reaction of ArN_2^+

In view of the established ability of ArN_2^+ to coordinate directly to transition metals to form arylazo complexes,[3,108,119,125-7,140,144-7,149] this initial step (Equation VII-1) had to be seriously considered.

$$[Ir(CO)Cl(PPh_3)_2] + ArN_2^+ \longrightarrow [Ir(CO)Cl(PPh_3)_2(N_2Ar)]^+ \quad (VII-1)$$

Evidence against arylazo complex formation in the benzene-ethanol (or benzene-_iso_-propanol) reaction medium leading to the complexes 4 and 5 was provided by the experimental findings, in each of which the reaction between an iridium (I) complex and ArN_2^+ afforded an arylazo complex when the solvent was acetone (Reactions VII-2a and VII-3a) or methanol-water (Reaction VII-4a), but failed to do so when the solvent was benzene-ethanol (Reactions VII-2b, VII-3b and VII-4b).

(c.f. Ref. 172)

$$[Ir(CO)Cl(PPh_3)_2] + ArN_2^+ \quad \begin{array}{l} \xrightarrow{\text{(a)}} [Ir(CO)Cl(PPh_3)_2N_2Ar]^+ \\ (CH_3)_2CO \qquad\qquad \underset{\sim}{2} \\[2em] \xrightarrow[C_6H_6-C_2H_5OH]{\text{(b)}} \text{No arylazo complex isolated} \end{array}$$

$$\underset{\underset{\sim}{1}}{}$$

(VII-2)

(c.f. Chap. VI)

$$[Ir(CO)Cl(PPh_3)_2] + ArN_2^+ \quad \begin{array}{l} \xrightarrow{\text{(a)}} [Ir(CO)Cl_2(PPh_3)_2N_2Ar] \\ (CH_3)_2CO \qquad\qquad \underset{\sim}{8} \\[2em] \xrightarrow[C_6H_6-C_2H_5OH]{\text{(b)}} \text{No arylazo complex isolated} \end{array}$$

$$\underset{\underset{\sim}{1}}{} \qquad +Cl^-$$

(VII-3)

(c.f. Ref. 144)

$$[Ir(CO)Cl(PMe_2Ph)_2] + ArN_2^+ \quad \begin{array}{l} \xrightarrow{\text{(a)}} [Ir(CO)Cl_2(PMe_2Ph)_2N_2Ar] \\ CH_3OH-H_2O \\[2em] \xrightarrow[C_6H_6-C_2H_5OH]{\text{(b)}} \text{No arylazo complex isolated} \end{array}$$

$$+Cl^-$$

(VII-4)

It is possible, of course, that the arylazo complexes formed in reactions VII-2(a), VII-3(a) and VII-4(a) were also formed in the reactions VII-2(b), VII-3(b) and VII-4(b), but were unstable in the $C_6H_6-C_2H_5OH$ medium. It was, in fact, found that the complex $\underset{\sim}{2}$, formed in reaction VII-2(a), was unstable in C_6H_6 solution, disproportionating to $\underset{\sim}{1}$ and ArN_2^+, and in $C_6H_6-C_6H_5OH$ medium formed both the aryltetrazene and aryldiimide complexes, $\underset{\sim}{4}$ and $\underset{\sim}{5}$, respectively:

$$[Ir(CO)Cl(PPh_3)_2(N_2Ar)]^+ \xrightarrow{\begin{array}{c} C_6H_6 \\ \\ C_6H_6-C_2H_5OH \end{array}} \begin{cases} [Ir(CO)Cl(PPh_3)_2] + ArN_2^+ \\ \underset{\sim}{1} \\ \\ [Ir(CO)(PPh_3)_2(N_4Ar_2)]^+ \\ \underset{\sim}{4} \end{cases}$$

$$\underset{\sim}{2}$$

$$\qquad \qquad \qquad \qquad \text{(VII-5)}$$

$$+ [IrCO)Cl(PPh_3)_2(HNNAr)]^+$$
$$\underset{\sim}{5}$$

However, the arylazo complexes formed in reactions VII-3(a) and VII-4(a) were found to be stable in $C_6H_6-C_2H_5OH$ medium, inferring that they are not formed at all in the reactions VII-3(b) and VII-4(b). The implications from these results are (a) that the solvent system is the crucial factor, and (b) that where the solvent system is $C_6H_6-C_2H_5OH$ the aryldiazonium ion either is not free to coordinate directly to iridium, or, once coordinated, undergoes further reaction.

Considering the known nucleophilicity[41] of Vaska's complex, $\underset{\sim}{1}$ and the electrophilic nature of ArN_2^+, direct coordination of $ArN_2^+(Ar=R-C_6H_4)$ to $Ir(I)$ might be expected to be enhanced by (a) increasing the electron withdrawing nature of the aryl substituent R (thus increasing the electrophilicity of the aryldiazonium cation) and (b) changing the triphenylphosphine ligands of $\underset{\sim}{1}$ to the more basic methyldiphenyl or dimethylphenylphosphine ligands (thus increasing the nucleophilicity of iridium).[41] In practice, the formation of the aryltetrazene complexes, $\underset{\sim}{4}$, was indeed favoured by R becoming more strongly electron withdrawing (c.f.

Table II-2), whereas for the aryldiimide complexes, $\underset{\sim}{5}$, the lowest yields were obtained for the strongly electron withdrawing substituents (c.f. Table II-1). For the PMePh$_2$ and PMe$_2$Ph analogues of $\underset{\sim}{1}$ neither $\underset{\sim}{4}$ nor $\underset{\sim}{5}$ were formed at all, indicating that formation of an arylazo adduct, if indeed it forms at all, does not occur by the anticipated nucleophilic attack of Ir(I) on ArN$_2^+$.

C. Evidence for hydride abstraction: the role of the solvent.

There is good evidence that hydride abstraction from the alcohol occurs during the reaction between Vaska's complex, $\underset{\sim}{1}$, and ArN$_2^+$ to give the complexes $\underset{\sim}{4}$ and $\underset{\sim}{5}$. Neither of these complexes was formed when ethanol was replaced by methanol, t-butanol, acetone, dichloromethane, nitromethane or acetic acid, but both were observed for iso-propanol which, like ethanol, has an activated α-hydrogen atom. Further, when ethanol was replaced by the better α-hydrogen donor, iso-propanol, a twenty percent higher yield of the aryltetrazene complex $\underset{\sim}{4}$b resulted, as ascertained from the molar absorptivity, ϵ 500nm.

Repeating the synthesis with C$_2$H$_5$OD had no observable effect, whereas substituting C$_2$D$_5$OD for C$_2$H$_5$OH caused a clearly observable drop in the rate of aryltetrazene formation, as followed spectroscopically by the change in ϵ_{500nm} with time (Diagram VII-1). Experimental difficulties did not allow the measurement of reliable approximate zero-time rates, so that no quantitative comparison of rate constants could be

Diagram VII-1   Comparison of the formation of the aryltetrazene complex $[Ir(CO)(PPh_3)_2\{N_4(C_6H_4\underline{p}\text{-}Br)_2\}]BF_4$, $\underset{\sim}{4}d$, in benzene-C_2H_5OH or benzene-C_2H_5OD)(curve A), and benzene-C_2D_5OD (curve B); $\underline{p}$-$BrC_6H_4N_2BF_4$ 0.031 mmole, $[Ir(CO)Cl(PPh_3)_2]$ 0.031 mmole, benzene 3.75 ml and alcohol 1.25 ml, at 25°C.

made. However, the results point in favour of a primary

isotope effect in C-H bond cleavage, presumably of an

α-hydrogen atom, viz:

$$RR^1C-O-H \longrightarrow RR^1C=O + H^+ + [H^-] \qquad (VII-6)$$
$$\overset{|}{H}$$

In agreement, acetone has been identified in the iso-propanol

reaction and acetaldehyde in the ethanol reaction.

D. Evidence for a common intermediate

That a common intermediate may be involved in the

mechanistic routes to both the aryltetrazene complexes, 4,

and the aryldiimide complexes, 5, is strongly implicated by

the fact that certain changes in the reaction conditions have

the same effect on the formation of both 4 and 5, as

exemplified by the following experimental observations:

(i) where the solvent medium was benzene-ethanol or

benzene-iso-propanol, both 4 and 5 were obtained;

conversely, when the ethanol (or iso-propanol)

was replaced by methanol, t-butanol, acetone,

dichloromethane, nitromethane or acetic acid

neither complex was obtained;

(ii) substitution of the triphenylphosphine ligands of

$[Ir(CO)Cl(PPh_3)_2]$, 1, by either methyldiphenyl-

phosphine or dimethylphenylphosphine ligands

prevented the formation of both 4 and 5;

(iii) where the substituent R on the aryldiazonium
cation, $R-C_6H_4N_2^+$, was a strong electron donor
(p-OH, p-NEt$_2$), the formation of both 4 and 5
was completely inhibited.

Further, for reactions in benzene-iso-propanol,
quantitative determinations of the acetone produced (see
Equation VII-6) suggest that α-hydride abstraction from the
alcohol contributes to the formation of both 4 and 5. These
results are summarised in Table VII-1, from which it can be
seen that in reactions 1 and 2 the yields of acetone correspond
closely to the combined yields of 4 and 5. The 2,6-difluoro-
phenyldiazonium ion in reaction 3 failed to yield either 4 or
5, yet acetone was recovered in comparable quantity indicating
that α-hydride abstraction had occurred, presumably leading
to an intermediate whose further reaction to give 4 and 5 was
hindered by the presence of the ortho-substituents.

E.   Nature of the common intermediate

Although α-hydride abstraction from the alcohol occurs
in the mechanism leading to the complexes 4 and 5, it is still
not clear at what stage the alcohol is involved in the
reaction, but three main possibilities exist, viz:

(i) α-hydride abstraction from the alcohol by Vaska's
complex, $[Ir(CO)Cl(PPh_3)_2]$ 1, as in Equation VII-7:

$$[Ir(CO)Cl(PPh_3)_2] + RR^1C\text{-}O\text{-}H \longrightarrow [Ir(CO)ClH_2(PPh_3)_2]$$
$$\underset{1}{} \qquad \overset{|}{H} \qquad \qquad + RR^1CO \qquad \qquad (VII-7)$$

Table VII-1

Yields of aryltetrazene complex ($\underset{\sim}{4}$),
ortho-metalated aryldiimide complex ($\underset{\sim}{5}$) and
acetone from reactions between Vaska's complex,
$[Ir(CO)Cl(PPh_3)_2]$ ($\underset{\sim}{1}$) and aryldiazonium tetrafluoroborate
in benzene-iso-propanol medium.

Reaction in C$_6$H$_6$-iso-propanol	Yield (mmole)		
	$\underset{\sim}{4}$	$\underset{\sim}{5}$	Acetone
1. p-BrC$_6$H$_4$N$_2^+$ + $\underset{\sim}{1}$	0.027	0.028	0.054
2. p-FC$_6$H$_4$N$_2^+$ + $\underset{\sim}{1}$	0.056	0.024	0.082
3. 2,6-F$_2$C$_6$H$_3$N$_2^+$ + $\underset{\sim}{1}$	nil	nil	0.082

This type of reaction has not been reported for Vaska's complex and, in agreement, no reaction at all was observed between 1 and either ethanol or iso-propanol (or benzene-ethanol or benzene-iso-propanol) even over prolonged periods at refluxing temperatures.

(ii) α-hydride abstraction from the alcohol by an electrophilic iridium complex, a type of reaction which has been reported[155-8] for both iridium (I) and iridium (III). Thus, for example, in the presence of diazonium ion, 1 may be converted to the iridium (III) arylazo complex cation $[Ir(CO)Cl(PPh_3)_2(N_2Ar)]^+$ 2 which, being coordinatively unsaturated, is a suitable candidate for α-hydride abstraction to give the hydride complex $[Ir(CO)HCl(PPh_3)_2(N_2Ar)]$:

$$[Ir(CO)Cl(PPh_3)_2] + ArN_2^+ \longrightarrow [Ir(CO)Cl(PPh_3)_2(N_2Ar)]^+ \xrightarrow{\overset{172}{H^-}}$$
$$\underset{1}{} \qquad\qquad\qquad \underset{2}{}$$

$$[Ir(CO)HCl(PPh_3)_2(N_2Ar)] \qquad\qquad (VII-8)$$

This particular proposal (Equation VII-8) can be considered doubtful on the basis that the arylazo complex cation 2 was found to be unstable in both benzene and benzene-ethanol media, disproportionating immediately to 1 and ArN_2^+. However, the possibility that some other electrophilic iridium species is effecting the hydride abstraction cannot be ignored, although no evidence for this occurring in the reaction leading to 4 and 5 has as yet been obtained. Attempts to detect an

intermediate iridium hydride species by infrared monitoring
of the reaction solution were negative, and examination of the
residual material after isolation of both $\underset{\sim}{4}$ and $\underset{\sim}{5}$ from the
reaction mixture provided no firm evidence for an iridium
hydride species.

(iii) α-hydride abstraction by electrophilic attack of
ArN_2^+ on the alcohol, yielding the unstable and highly reactive
intermediate aryldiazene,[159-163] $ArN=NH$:

$$RR'-\overset{\overset{\displaystyle H}{\overset{\displaystyle |}{\underset{\curvearrowright}{O}}}}{\underset{|}{C}}-H + N\equiv N-Ar \longrightarrow RR'C=O + [Ar-N=N-H] + H^+ \qquad (VII-9)$$

Certain experimental observations favour this mode of hydride
abstraction over those presented in (i) and (ii). When
$\underline{p}$-$FC_6H_4N_2BF_4$ was stirred at room temperature in ethanol (or
$\underline{iso}$-propanol) a small amount of acetaldehyde (or acetone) was
produced, whereas, as previously mentioned, no reaction was
observed between Vaska's complex and either ethanol or $\underline{iso}$-
propanol under a variety of conditions. The production of
acetaldehyde from ArN_2^+ and ethanol is well documented,[171] as
is the formation of aryldiazene, $ArN=NH$, in the hydride
reduction of aryldiazonium ions.[161,162,164,166,167] By
allowing Vaska's complex ($\underset{\sim}{1}$) and $C_6H_5N_2BF_4$ to react in benzene-
ethanol medium in the presence of added $C_6H_5N=NH$, the yield of
phenyltetrazene complex ($\underset{\sim}{4a}$), as determined spectroscopically
from $\epsilon_{500\ nm}$, was increased by twenty percent over that obtained
in the absence of added $C_6H_5N=NH$. Earlier observations, such

as the requirement for the substituent R in $RC_6H_4N_2^+$ being
electron withdrawing in nature, and the non-formation of either
4 or 5 when the triphenylphosphine ligands of 1 were replaced
by the more basic methyldiphenyl or dimethylphenylphosphine
ligands are in keeping with the involvement of an aryldiazene
intermediate. Thus, the ability of ArN_2^+ to abstract H^- from
a suitable alcohol (c.f. Equation VII-9) should be enhanced
by an electron withdrawing aryl substituent, whereas the ability
of an iridium complex to abstract H^- should be decreased by
the presence of the less basic (PPh_3) ligands.[157,165] Further,
coordination to iridium of the nucleophilic ArN=NH species
should be more favoured by the less basic triphenylphosphine
ligands than would coordination of the electrophilic ArN_2^+
species.

From the foregoing results and discussion it can be
concluded that the role of the ethanol or iso-propanol is to
provide a source of hydride ion, H^-, and, somewhat tentatively,
that the H^- effects the reduction of the aryldiazonium cation
to the highly reactive aryldiazene intermediate, ArN=NH,
whose further reaction leads to the complexes 4 and 5 (Equation
VII-10), as discussed in Section F.

$$ArN \equiv N^+ \quad \underset{H}{\overset{R \quad R'}{C-O-H}} \xrightarrow{C_6H_5} [ArN=NH] + H^+ + RR''C=O \qquad (VII-10)$$

$$\underset{4}{\overset{1}{\nearrow}} \qquad \underset{5}{\overset{1}{\searrow}}$$

F. Proposed mechanisms

Accepting that [ArN=NH] is the initially formed common intermediate when Vaska's complex $\underset{\sim}{1}$ and ArN_2^+ are allowed to react in benzene-ethanol or benzene-$\underline{iso}$-propanol, three feasible mechanisms (A, B and C in Scheme VII-1) can be proposed. Mechanisms A and B lead to the aryltetrazene complexes, $\underset{\sim}{4}$, and C to the $\underline{ortho}$-metalated aryldiimide complexes, $\underset{\sim}{5}$. In A, step (1) envisages coupling between ArN_2^+ and the aryldiazene intermediate, ArN=NH (or the diazenyl anion, ArN=N$^-$, which is a stronger nucleophile than undissociated ArN=NH),[160,161] to give the free tetrazadiene ligand [ArN=N-N=NAr]. That the diazonium cation will couple with all manner of nitrogen compounds having an N-attached hydrogen is well established,[168(a)] but no simple tetrazadienes, R-N=N-N=N-R, have been reported;[b] the synthesis of the aryltetrazene complexes, $\underset{\sim}{4}$, from $\underset{\sim}{1}$ and ArN_2^+ may represent an example of the stabilization of this highly reactive intermediate by its oxidative addition to $\underset{\sim}{1}$ (step (2), mechanism A and step (4), mechanism B). On the other hand, formation of the free tetrazadiene may well be thermodynamically unlikely, and an alternative reaction of the aryldiazene - intermediate, ArN=NH, is Lewis base addition to the iridium of Vaska's complex to form the aryldiimide complex [Ir(CO)Cl(PPh$_3$)$_2$(HN=NAr)], as depicted by step (1) in mechanism B (Scheme VII-1). Coupling then occurs (step (2), mechanism B) between ArN_2^+ and the

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b. Substances that can be considered as formally derived from such a structure are known in the form of N-azido amines, $R_2N-N_3 \longleftrightarrow R_2\overset{+}{N}=N-N=\overset{-}{N}$.[168b]

$$ArN_2^+BF_4^- + RR'CHOH \xrightarrow{C_6H_6} [ArN=NH \rightleftharpoons ArN=N^-H^+] + H^+BF_4^- + RR'CO$$

A $\qquad$ B $\qquad$ C

(1) ArN_2^+ (A) $\qquad$ (1) $\underset{\sim}{1}$ (B) $\qquad$ (1) $\underset{\sim}{1}$ (C)

$$[ArN=\overset{H}{\overset{|}{N}}^+N=NAr] \rightleftharpoons [ArN=N-N=NAr]H^+$$

(2) $\underset{\sim}{1}$
$-HCl$

$$\left[\underset{Ar}{\overset{H}{\underset{N}{\overset{|}{N}}}}{=}N-Ir(CO)ClP_2\right] \rightleftharpoons \left[\overset{ArN_{\diagdown}}{\underset{H-Ir(CO)ClP_2}{N}}\right]$$

(2) $\begin{array}{c}ArN_2^+ \\ -HCl\end{array}$ $\qquad$ (2) $\begin{array}{c}\text{o-metalation} \\ -H_2\end{array}$

$$\left[\overset{ArN=N_{\diagdown}}{\underset{ArN^{\diagup}}{N^+}}{-}Ir(CO)P_2\right] \qquad \overset{N\diagup N}{\diagdown}Ir(CO)ClP_2 \quad \underset{\sim}{\underset{6}{}}$$

(3) $\qquad$ (3) H^+

$$\left[\overset{Ar}{\underset{N}{\overset{|}{\underset{N}{\overset{N=N}{\diagdown}}}}}{\underset{Ar}{\overset{}{N^+}}}{-}Ir(CO)P_2\right] \qquad \left[\overset{H}{\underset{N}{\overset{N}{\diagdown}}}Ir(CO)ClP_2\right]^+ \quad \underset{\sim}{\underset{5}{}}$$

(4)

$$\overset{Ar}{\underset{N}{\overset{|}{\underset{N}{\overset{N}{\diagdown}}}}}{\underset{Ar}{\overset{N}{\underset{N}{\overset{+}{\cdot}}}}}Ir(CO)P_2$$

$\underset{\sim}{\underset{4}{}}$

Scheme VII-1 Proposed mechanistic routes A, B and C for the formation of the aryltetrazene complexes ($\underset{\sim}{4}$) and the ortho-metalated diimide complexes ($\underset{\sim}{5}$): $\underset{\sim}{1}$ represents Vaska's complex, $[Ir(CO)Cl(PPh_3)_2]$, and P represents triphenylphosphine, PPh_3.

coordinated aryldiazene with elimination of H^+ and Cl^- to give a monohaptotetrazadiene complex cation. Sigma-bond migration accompanied by chelation and electron rearrangement (steps(3) and (4), mechanism B) yields the delocalised iridium (III) aryltetrazene complex cation, 4.

Mechanism C, leading to the ortho-metalated aryldiimide complexes, 5, invokes, as step (1), oxidative addition of the aryldiazene intermediate to Vaska's complex, 1, giving a six-coordinate iridium(III) hydride arylazo complex $[Ir(CO)HCl(PPh_3)_2(N_2Ar)]$ which may be in coexistence with $[Ir(CO)Cl(PPh_3)_2HNNAr]$ (step (1), mechanism B), constituting an insertion process. In step (2) (mechanism C) the hydride arylazo complex is envisaged as undergoing ortho-metalation via electrophilic attack by iridium(III) on the aromatic ring[74,88] to yield the known complex 6 (c.f. Chapter IV). The ortho-metalated aryldiazene cation, 5, is readily obtained by protonation of 6 with H^+ (step 3); that this protonation step occurs smoothly has previously been demonstrated, as discussed in Chapters III and IV.

In an attempt to verify the existence of the hydride intermediate, $[Ir(CO)HCl(PPh_3)_2N_2Ar]$, formed in step (1), mechanism C, the reaction between 1 and ArN_2^+ in C_6H_6-EtOH was attempted using aryldiazonium salts blocked in both ortho-positions to prevent step (2) (ortho-metalation of the arylazo ring) from occurring. Unfortunately, pure products could not be isolated from these reactions: in each case, for the 2,6-

difluoro, 2,6-dimethyl, and 2-chloro, 4-bromo, 6-iodo phenyl-
diazonium tetrafluoroborates, the residual solid after
evaporation of solvent from the reaction mixture exhibited an
infrared absorption at ~3150cm^{-1} attributable to ν_{N-H}, but no
absorptions attributable to an iridium hydride bond were
observed. Attempted purification of the products resulted in
loss of the infrared absorption at 3150cm^{-1}. Nevertheless, the
initial indication of a species containing an N-H function, and
the apparent absence of an iridium hydride species, infers (a) the
possible formation of an aryldiazene adduct, [Ir(CO)Cl(PPh$_3$)$_2$
(HN=NAr)] (step 1, mechanism 8), or that $\underline{ortho}$-metalation may
have taken place (despite blocking of the $\underline{ortho}$-positions of the
arylazo ring), presumably via the triphenylphosphine ligands.

Indirect evidence for the participation of the triphenyl-
phosphine ligands in the $\underline{ortho}$-metalation process was obtained
by carrying out the reaction with deuterated reagents, originally
with the intention of synthesising the deutero-analogue,
[Ir(CO)Cl(PPh$_3$)$_2$(DN=NAr)]BF$_4$, of the complexes 5; the purpose
behind this was to locate the source of the diimide (N-H) proton.
Thus, when the syntheses were performed under the following
conditions: (a) C$_2$H$_5$OH replaced by C$_2$H$_5$OD; (b) C$_2$H$_5$OH replaced
by C$_2$D$_5$OD; (c) C$_6$H$_5$N$_2$BF$_4$ replaced by C$_6$D$_5$N$_2$BF$_4$; (d) both C$_2$H$_5$OH
and C$_6$H$_5$N$_2$BF$_4$ replaced by C$_2$D$_5$OD and C$_6$D$_5$N$_2$BF$_4$, respectively,
and (e) both C$_6$H$_6$ and C$_2$H$_5$OH replaced by C$_6$D$_6$ and C$_2$D$_5$OD respec-
tively, only an N-H stretching frequency and no N-D stretching
frequency in the infrared was obtained in each case, failing
to show whether the N-H proton originated from the

hydroxyl proton of ethanol (condition (a)), the
α-proton of ethanol (condition (b)), the arylazo ring
(conditions (c) and (d)) or benzene (condition (e)).
This inability to synthesise a deutero (N-D) analogue of
the aryldiimide complexes, 5, can be explained by invoking
a reversible ortho-metalation process occurring in solution
and involving both the aryldiimide and the triphenylphosphine
ligands (c.f. Equation VII-11), the equilibrium concentration
of the ortho-bonded species being high. Thus, the 14 available
ortho-positions are involved in the ortho-metalation process,
resulting in scrambling among the 14 ortho-protons and the
acidic diimide (N-H) proton. Some evidence for this was

$$(VII-11)$$

provided by stirring a solution of the p-bromophenyl diimide
complex, 5d, in C_2H_5OH for six hours under an atmosphere of D_2
at room temperature; this resulted in a p-bromophenyldiimide
complex exhibiting both a medium intensity absorption at
3150 cm^{-1} and a weak intensity absorption at 2310 cm^{-1},

attributable to ν_{N-H} and ν_{N-D}, respectively. When this partially deuterated complex was redissolved, this time in CH_3OD, and stirred for a further six hours under an atmosphere of D_2 at room temperature, only a slight increase was observed in the intensity of ν_{N-D} of the isolated complex, suggesting exchange with deuterium to be slow; this is in keeping with the equilibrium concentration of the ortho-bonded species being high (c.f. Equations VII-11 and VII-12).

Unfortunately, no evidence could be found in either the mass spectrum or the infrared spectrum for deuterium incorporation in the aromatic rings. Facile equilibria of the type

$$L_m(P)_n M \overset{P}{\underset{}{\diagup}} \quad \underset{\longleftarrow}{\overset{H_2}{\longrightarrow}} \quad L_m(P)_{n+1} MH$$

($P = PPh_3$ or $P(OC_6H_5)_3$; M=Rh, Ru, Co, Ir) have been demonstrated[86,88,169,170] for certain ortho-metalated complexes by exchange with deuterium, and the existence of this type of equilibrium in solutions of 5 (c.f. Equation VII-12) can be inferred from the above results.

To summarise, the only firm conclusion which can be drawn from the foregoing results and discussion is that, when $[Ir(CO)Cl(PPh_3)_2]$ (1) and ArN_2BF_4 are allowed to react together in either benzene-ethanol or benzene-iso-propanol to form the complexes 4 and 5, the function of the alcohol is as a hydride ion (H^-) donor. Also, from (a) the amounts of acetone produced in the reactions involving iso-propanol (c.f. Table VII-1) and

$$(PPh_3)_2Cl(CO)Ir \overset{D_2}{\underset{-D_2}{\rightleftharpoons}} (PPh_3)_2Cl(CO)Ir \qquad (VII-12)^b$$

$$(PPh_3)_2Cl(CO)Ir \overset{H_2}{\underset{-H_2}{\rightleftharpoons}} (PPh_3)_2Cl(CO)Ir$$

(b) the non-formation of 4 or 5 when solvents other than
ethanol or iso-propanol were used, it can be inferred with some
degree of confidence that the H-donating alcohol is required
for the formation of both 4 and 5. Further, the evidence
presented points to the involvement of a common intermediate
leading to 4 and 5. Although the exact nature of the inter-
mediate is still uncertain, the current data suggest the free
aryldiazene, ArN=NH, or a species resulting from reaction
between ArN=NH and an iridium complex.

b. Participation of PPh₃ ligands omitted for simplicity.

CHAPTER VIII

Experimental Procedures

A. Instrumentation and Materials

1. Instrumentation utilised

Infrared spectra, on samples pressed in KBr, were recorded on a Perkin Elmer 457 spectrometer for routine spectra and on a Beckman IR 12 spectrometer for accurate wavenumber calibrations ($\pm 1 cm^{-1}$).

Raman spectra ($\pm 1 cm^{-1}$), on solid samples at room temperature, were recorded using a Cary 81 spectrometer with unfocussed He-Ne laser excitation from a Spectra-Physics Model 125 laser producing 70 mW at source.

Proton n.m.r. spectra were recorded at 60 MHz and 100 MHz using Varian A-56/60 and XL-100 spectrometers: results are reported as τ using $(CH_3)_4Si$ as internal standard ($\tau = 10$).

^{19}F n.m.r. spectra were recorded at 56.4 MHz using a Varian A-56/60 spectrometer: results are reported as Hz, relative to CCl_3F as internal standard

Electronic spectra were recorded on a Unicam SP800 spectrometer using quartz cells.

Magnetic susceptibility measurements were made at room temperature on a Faraday apparatus calibrated against $HgCo(NCS)_4$.

Electrical conductances were determined at room
temperature using a Radiometer (Copenhagen) type GHM2
conductivity meter. The cell constant (k) was determined
as 0.0958cm^{-1}.

pKa values were determined by potentiometrically
titrating 10^{-4} M ethanolic solutions of the appropriate
complexes against 2×10^{-4} M ethanolic KOH using a Radiometer
(Copenhagen) pH meter 4d. Titration curves were obtained
by plotting pH against V, and accurate equivalence points
were ascertained by plotting ΔpH/ΔV against ΔV (V=volume of
2×10^{-4}M KOH). The pKa values were obtained from the
relationship, pKa=pH at half the equivalence point.

Quantitative determination of the gases, CO and N_2,
evolved on pyrolysis of the aryltetrazene complex 4b was
achieved by heating 35.8 μgm of 4b for 3 hours at 550°C in
a sealed, evacuated tube. The resulting gases were allowed
to pass through a glass coil at liquid-nitrogen temperature,
and the non-condensible gases collected in a capillary
tube using a Toepler system. The non-condensible gases were
assayed for N_2 and CO by gas chromatography on a Porapak Q
column (standardised for N_2 and CO) at -78°C with He as the
carrier gas.

Elemental analyses were determined by the micro-
analytical laboratory at Simon Fraser University and by
A. Bernhardt, Germany.

2. Materials supplied

The complexes $[Ir(CO)Cl(PPh_3)_2]$, $[Ir(CO)Br(PPh_3)_2]$, $[Ir(CO)I(PPh_3)_2]$, $[Ir(CO)Cl(PMePh_2)_2]$ and $[Ir(CO)Cl(PMe_2Ph)_2]$ were purchased from Strem Chemicals, Inc., Danvers, Mass., U.S.A. They were used without further purification.

B. Syntheses and Reactions

1. Preparation of aryldiazonium tetrafluoroborates, ArN_2BF_4.

All of the diazonium salts were prepared from the corresponding aniline as described by A. Roe[173] according to the following reaction sequence:

$$R-C_6H_4-NH_2 + HBF_4 \xrightarrow{H_2O} R-C_6H_4-NH_3^+BF_4^-$$

$$NaNO_2 + HBF_4 \xrightarrow{H_2O} HNO_2 + NaBF_4$$

$$HNO_2 + R-C_6H_4-NH_3^+ \xrightarrow{H_2O} R-C_6H_4-N\equiv N^+ + 2H_2O$$
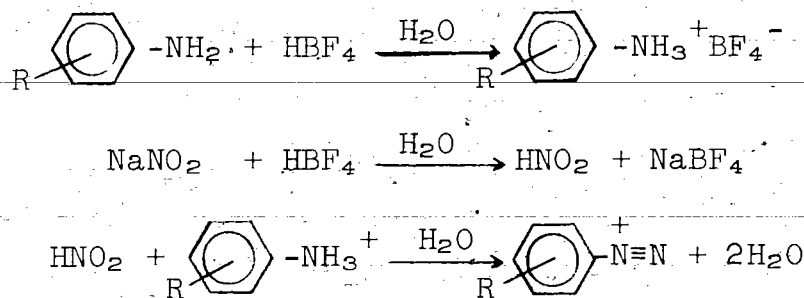
As an example, the preparation of p-methoxyphenyldiazonium tetrafluoroborate, $p-CH_3OC_6H_4N_2BF_4$, is described: 48% aqueous HBF_4 (9.2 ml) was transferred to a 100 ml beaker and diluted with water (9.2 ml). p-Anisidine (3.1g) was added, with stirring, and the mixture was cooled to 0°C in an ice-bath. Diazotization was accomplished by adding dropwise, and with stirring, a cooled (0°C) solution of $NaNO_2$ (1.75g) in

water (3.5ml). During diazotization the temperature was maintained at not higher than 10°C. After complete addition of the NaNO$_2$ solution, the presence of excess nitrous acid was ensured by testing with starch-KI paper, and the solid product[a] isolated by suction filtration through a sintered glass funnel. The product was washed with (a) cold 5% aqueous HBF$_4$, (b) cold methanol and (c) diethylether, and then recrystallised from acetone-ether.[b] The infrared spectrum of each diazonium salt thus prepared was recorded and the accurate (± 1 cm^{-1}) $\nu_{N \equiv N}^+$ values are listed in Appendix B.

2. Syntheses of the aryltetrazene complexes
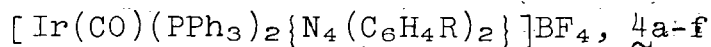
[Ir(CO)(PPh$_3$)$_2${N$_4$(C$_6$H$_4$R)$_2$}]BF$_4$, $\underset{\sim}{4}$a-f

In the following methods, (a) all procedures were carried out under an atmosphere of argon, unless otherwise noted, and (b) the benzene-ethanol media can be replaced by benzene-iso-propanol.

(i) Preparation of $\underset{\sim}{4}$b (R=p-F)

Method A. [Ir(CO)Cl(PPh$_3$)$_2$], $\underset{\sim}{1}$ (0.125mM, 97.6mg) was dissolved, with stirring, in benzene (15ml) at room temperature. p-FC$_6$H$_4$N$_2$BF$_4$ (0.125 mM, 26.3 mg) was added, followed immediately by absolute ethanol (1.5 ml). The mixture was

(a) If a solid product has not appeared at this stage, precipitation can be induced by the addition of a small amount of solid NH$_4$BF$_4$ or NaBF$_4$.

(b) All of the aryldiazonium salts were recrystallised from acetone-ether except for p-CF$_3$C$_6$H$_4$N$_2$BF$_4$, in which case recrystallisation was effected from methanol-ether.

stirred for 1 hour, and the resulting red solution was reduced
in vacuo to approximately half its volume. Benzene (10 ml)
was added to this solution and crystallization of the product,
$[Ir(CO)(PPh_3)_2\{N_4(C_6H_4p-F)_2\}]BF_4 \cdot C_6H_6$, induced by storing at
+5°C. The red crystals were isolated by filtration under
argon pressure, washed with benzene and then with diethylether,
and dried in vacuo. The product can be recrystallized from
either acetone-ether or acetone-benzene.

Method B. In this method, the red solution obtained
after stirring the reagents for 1 hour, as in Method A, was
freeze-dried to completely remove the solvent. The residual
red-orange solid was stirred in benzene (15 ml) for 2 hours,
and the resulting brick-red, insoluble solid filtered-off
and washed with benzene. On recrystallization of this solid
from acetone-benzene (acetone-ether is also suitable), red
crystals of the product, $[Ir(CO)(PPh_3)_2\{N_4(C_6H_4p-F)_2\}]BF_4 \cdot C_6H_6$
were obtained. Both methods A and B provided a similar yield
(Table II-2) of 4b.

(ii) Preparation of 4c (R = p-Cl)

This preparation was best performed by method (i)A,
using p-$ClC_6H_4N_2BF_4$ in lieu of p-$FC_6H_4N_2BF_4$.

(iii) Preparation of 4a (R = H)

This preparation was performed by method (i)B, using
$C_6H_5N_2BF_4$ in place of p-$FC_6H_4N_2BF_4$. In this case, when
the residual solid from removal of solvent from the reaction
solution was stirred with benzene (15 ml) for 2 hours, a red,
tarry, insoluble material resulted. Acetone was added to

the benzene/tar mixture until complete dissolution occurred.
This red solution was reduced in volume, _in vacuo_, until
precipitation just started, and then was cooled to +5°C.
The resulting brick-red solid was filtered off, and
recrystallised from acetone-ether, providing red crystals
of the product $[Ir(CO)PPh_3)_2\{N_4(C_6H_5)_2\}]BF_4$.

(iv) Preparation of 4e (R = p-CF₃)

This preparation was performed by method (i)B,
substituting $\underline{p}-CF_3C_6H_4N_2BF_4$ for $\underline{p}-FC_6H_4N_2BF_4$.

(v) Preparation of 4d (R = p-Br)

This preparation was performed by method (i)B,
substituting $\underline{p}-BrC_6H_4N_2BF_4$ for $\underline{p}-FC_6H_4N_2BF_4$, and using 5 ml
absolute ethanol instead of 1.5 ml. The brick-red solid
obtained by stirring the freeze-dried solid in benzene (15 ml)
for two hours was recrystallized from acetone-ether as follows:
the solid was dissolved in the minimum amount of acetone,
and diethyl ether added drop-wise until the solution became
just cloudy. The yellow crystals which formed on allowing
this solution to sit at room temperature were filtered off
and were shown to be the _ortho_-metalated aryldiimide complex,
5e. The red filtrate was stirred at +5°C until crystallization
occurred. The resulting red crystals of the aryltetrazene
complex $[Ir(CO)(PPh_3)_2\{N_4(C_6H_4\underline{p}-Br)_2\}]BF_4$ were filtered off,
washed with ether and dried _in vacuo_.

(vi) Preparation of 4f (R = p-OCH$_3$)

[Ir(CO)Cl(PPh$_3$)$_2$], 1 (0.125 mM, 97.6 mg) was dissolved, with stirring, in benzene (15 ml) at room temperature. p-CH$_3$OC$_6$H$_4$N$_2$BF$_4$ (0.125 mM, 27.9 mg) was added, followed immediately by absolute ethanol (1.5 ml). The mixture was stirred for 1 hour and the resulting reddish-orange solution filtered to remove unreacted diazonium salt (70% recovery). Solvent was completely removed from the filtrate by a freeze-drying procedure, and the reddish-orange residual solid stirred with 3 ml acetone for 5 minutes. The precipitated yellow solid, impure Vaska's complex, 1, was removed by filtration. The red acetone solution was evaporated to approximately 1 ml, and further precipitated 1 filtered off. Diethyl ether (10 ml) was added to the filtrate and the precipitated red, solid complex [Ir(CO)(PPh$_3$)$_2${N$_4$(C$_6$H$_4$p-OCH$_3$)}]BF$_4$ isolated by filtration, washed with diethyl ether and dried in vacuo.

3. Syntheses of the ortho-metalated aryldiimide complexes
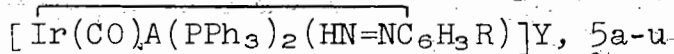
[Ir(CO)A(PPh$_3$)$_2$(HN=NC$_6$H$_3$R)]Y, 5a-u

In the following methods, (a) all procedures were carried out under an atmosphere of argon, unless otherwise noted, and (b) the benzene-ethanol media can be replaced by benzene-iso-propanol.

(i) Preparation of 5a (R = H, A = Cl, Y = BF$_4$)

[Ir(CO)Cl(PPh$_3$)$_2$], 1, (0.125 mM, 97.6 mg) was dissolved, with stirring, in benzene (15 ml) at room temperature. C$_6$H$_5$N$_2$BF$_4$ (0.125 mM, 24.0 mg) was added, followed immediately

by absolute ethanol (5 ml). The mixture was stirred for 3 hours and the resulting orange-red solution evaporated to dryness by a freeze-drying procedure. The residual solid was stirred in benzene (15 ml) for 2 hours, and the insoluble material resulting from this filtered-off (under argon pressure), washed with benzene, and then with diethyl ether, and recrystallized as follows: the crude solid was dissolved in the minimum amount of acetone, and diethyl ether added until the solution was just cloudy. This solution was allowed to sit at room temperature until precipitation of the yellow, crystalline product, $[Ir(CO)Cl(PPh_3)_2(HN=NC_6H_4)]BF_4$, occurred (it is important that this recrystallisation is performed carefully as the addition of too much diethyl ether, or cooling of the solution, may induce co-precipitation of the red phenyltetrazene complex, 4a). The yellow crystals were filtered off, washed with diethyl ether containing a small amount of acetone and dried in vacuo. The tetrazene complex, 4a, usually in small yield, can be obtained from the filtrate by storing it at +5°C until crystallization occurs.

(ii) Preparation of 5b (R = p-F, A = Cl, Y = BF_4)

This preparation was performed exactly as in 3(i), substituting p-$FC_6H_4N_2BF_4$ for $C_6H_5N_2BF_4$.

(iii) Preparation of 5c (R = p-Cl, A=Cl, Y = BF_4)

This preparation was performed exactly as in 3(i), substituting p-$ClC_6H_4N_2BF_4$ for $C_6H_5N_2BF_4$.

(iv) Preparation of 5d (R = p-CH$_3$, A = Cl, Y = BF$_4$)

This preparation was performed exactly as in 3(i), substituting p-CH$_3$C$_6$H$_4$N$_2$BF$_4$ for C$_6$H$_5$N$_2$BF$_4$.

(v) Preparation of 5e (R = p-Br, A = Cl, Y = BF$_4$)

This preparation was performed exactly as in 3(i), substituting p-BrC$_6$H$_4$N$_2$BF$_4$ for C$_6$H$_5$N$_2$BF$_4$.

(vi) Preparation of 5f (R = p-NO$_2$, A = Cl, Y = BF$_4$)

This preparation was essentially the same as in 3(i), apart from the following:

(a) p-NO$_2$C$_6$H$_4$BF$_4$ was used in lieu of C$_6$H$_5$N$_2$BF$_4$;

(b) the solid material obtained by freeze-drying the reaction solution was stirred in benzene (15 ml) for 2 hours and then filtered, as in 3(i), but the solid thus isolated was not the desired product and was discarded. Diethyl ether was added to the red filtrate until a cloudiness just appeared, and this was stored at +5°C for 24 hours. The greenish-yellow solid which precipitated out was filtered off, washed with diethyl ether containing a small amount of acetone and dried in vacuo; this was the desired product, 5f.

(vii) Preparation of 5g (R = p-CF$_3$, A = Cl, Y = BF$_4$)

This preparation was essentially the same as in 3(i), apart from the following changes:

(a) p-CF$_3$C$_6$H$_4$N$_2$BF$_4$ was used in lieu of C$_6$H$_5$N$_2$BF$_4$;

(b) the solid material obtained by freeze-drying the
reaction solution was stirred in benzene (15 ml)
for 2 hours and then filtered, as in 3(i). The
orange solid thus obtained was washed with benzene,
then with diethyl ether and recrystallised by dissol-
ving in 3 ml acetone, adding 12 ml diethyl ether and
allowing to stand at room temperature until
crystallisation occurred. The red crystalline solid,
isolated by filtration, was shown to be the aryl-
tetrazene complex, 4e, (and not the aryldiimide
complex, 5g). The desired product, 5g, was obtained
as a yellow-brown crystalline solid by adding ~10 ml
of diethyl ether to the yellow filtrate, cooling to
+5°C and filtering. The product was washed with
diethyl ether containing a small amount of acetone,
and dried in vacuo.

(vii) Preparation of 5h (R = o-F, A = Cl, Y = BF_4)
This preparation was performed exactly as in 3(i),
substituting o-$FC_6H_4N_2BF_4$ for $C_6H_5N_2BF_4$.

(ix) Preparation of 5i (R = o-Cl, A = Cl, Y = BF_4)
This preparation was performed exactly as in 3(i),
substituting o-$ClC_6H_4N_2BF_4$ for $C_6H_5N_2BF_4$.

(x) Preparation of 5j (R = o-Br, A = Cl, Y = BF_4)
This preparation was performed exactly as in 3(i),
substituting o-$BrC_6H_4N_2BF_4$ for $C_6H_5N_2BF_4$.

(xi) Preparation of 5k (R = o-NO₂, A = Cl, Y = BF₄) -

This preparation was performed exactly as in 3(i),

substituting o-NO₂C₆H₄N₂BF₄ for C₆H₅N₂BF₄.

(xii) Preparation of 5l (R = m-CH₃, A = Cl, Y = BF₄)

This preparation was essentially the same as in 3(i),

apart from the following:

(a) m-CH₃C₆H₄N₂BF₄ was substituted for C₆H₅N₂BF₄;

(b) the solid material obtained by freeze-drying the

reaction solution was dissolved in acetone (4 ml)

and the precipitated yellow Vaska's complex, 1

(20 mg), removed by filtration. Diethyl ether was

added to the red-orange filtrate until precipitation

just started, and this was stored at +5°C for 2 days.

The brown-orange solid precipitate, shown to be the

desired product, 5l, was filtered-off, washed with

diethyl ether containing a small amount of acetone,

and dried in vacuo.

(xiii) Preparation of 5m (R = m-OCH₃, A = Cl, Y = BF₄)

This preparation was performed exactly as in 3(i),

substituting m-CH₃OC₆H₄N₂BF₄ for C₆H₅N₂BF₄.

(xiv) Preparation of 5n (R = m-Br, A = Cl, Y = BF₄)

This preparation was essentially the same as in 3(i),

apart from the following:

(a) m-BrC₆H₄N₂BF₄ was substituted for C₆H₅N₂BF₄;

(b) the solid material obtained by freeze-drying the

reaction solution was stirred for 2 hours in benzene

(xi) Preparation of 5k (R = o-NO_2, A = Cl, Y = BF_4) -

This preparation was performed exactly as in 3(i),

substituting o-$NO_2C_6H_4N_2BF_4$ for $C_6H_5N_2BF_4$.

(xii) Preparation of 5l (R = m-CH_3, A = Cl, Y = BF_4)

This preparation was essentially the same as in 3(i),

apart from the following:

(a) m-$CH_3C_6H_4N_2BF_4$ was substituted for $C_6H_5N_2BF_4$;

(b) the solid material obtained by freeze-drying the

reaction solution was dissolved in acetone (4 ml)

and the precipitated yellow Vaska's complex, 1

(20 mg), removed by filtration. Diethyl ether was

added to the red-orange filtrate until precipitation

just started, and this was stored at +5°C for 2 days.

The brown-orange solid precipitate, shown to be the

desired product, 5l, was filtered-off, washed with

diethyl ether containing a small amount of acetone,

and dried in vacuo.

(xiii) Preparation of 5m (R = m-OCH_3, A = Cl, Y = BF_4)

This preparation was performed exactly as in 3(i),

substituting m-$CH_3OC_6H_4N_2BF_4$ for $C_6H_5N_2BF_4$.

(xiv) Preparation of 5n (R = m-Br, A = Cl, Y = BF_4)

This preparation was essentially the same as in 3(i),

apart from the following:

(a) m-$BrC_6H_4N_2BF_4$ was substituted for $C_6H_5N_2BF_4$;

(b) the solid material obtained by freeze-drying the

reaction solution was stirred for 2 hours in benzene

(15 ml) in which it completely dissolved. Diethyl
ether was added to this benzene solution until
precipitation just started, and this was allowed to
sit at room temperature until precipitation appeared
complete. The yellow-orange solid product, 5n, was
filtered-off, washed with diethyl ether containing
a small amount of benzene and dried in vacuo.

(xv) Preparation of 5o (R = m-Cl, A = Cl, Y = BF$_4$)

This preparation was performed exactly as in 3(i),
substituting m-ClC$_6$H$_4$N$_2$BF$_4$ for C$_6$H$_5$N$_2$BF$_4$.

(xvi) Preparation of 5p (R = m-NO$_2$, A = Cl, Y = BF$_4$)

This preparation was performed exactly as in 3(xiv),
substituting m-O$_2$NC$_6$H$_4$N$_2$BF$_4$ for m-BrC$_6$H$_4$N$_2$BF$_4$.

(xvii) Preparation of 5q (R = m-F, A = Cl, Y = BF$_4$)

This preparation was performed exactly as in 3(i),
substituting m-FC$_6$H$_4$N$_2$BF$_4$ for C$_6$H$_5$N$_2$BF$_4$.

(xviii) Preparation of 5r (R = o-Br, A = F, Y = BF$_4$)

This preparation involved (a) the synthesis and isolation
of [Ir(CO)F(PPh$_3$)$_2$], as described by Peone[42], followed by (b)
its reaction with o-Br C$_6$H$_4$N$_2$BF$_4$ in benzene-ethanol.

(a) Preparation of [Ir(CO)F(PPh$_3$)$_2$]

[Ir(CO)Cl(PPh$_3$)$_2$], 1 (0.15 mM, 117 mg) was added
to 30 ml of a saturated solution of NH$_4$F. The
resulting yellow suspension was heated to boiling
on a water bath with constant stirring; dissolution

of 1 was incomplete. To the refluxing mixture, Ag_2CO_3 (0.075 mM, 20.7 mg) was added and boiling was continued for $1\frac{1}{2}$ minutes. The hot suspension (containing precipitated AgCl) was then filtered into 30 ml of 0.1M aqueous NH_4F. A light yellow precipitate formed as the yellow filtrate mixed with the NH_4F solution. The yellow product was filtered, washed with distilled water and dried in vacuo. The yield of the product, $[Ir(CO)F(PPh_3)_2]$, was 96.8 mg (84.5%), and its infrared spectrum agreed with that reported by Peone.[42]

(b) Reaction of $[Ir(CO)F(PPh_3)_2]$ with $o\text{-}BrC_6H_4N_2BF_4$.

$[Ir(CO)F(PPh_3)_2]$ (0.125 mM, 95.4 mg) was stirred with benzene (15 ml), in which it was incompletely soluble. To this solution-suspension, $o\text{-}BrC_6H_4N_2BF_4$ (0.125 mM, 33.8 mg) was added, followed immediately by absolute ethanol (5 ml). The mixture was stirred for 3 hours and the resulting orange-red solution evaporated to dryness by a freeze-drying procedure. The red-orange residual solid was dissolved in the minimum volume of acetone, and diethyl ether added until the solution became just cloudy. The solution was allowed to sit at $+3°C$ for 4 hours, during which time orange crystals of the product, 5r, precipitated out. The orange crystals were filtered-off, washed with diethyl ether containing a small amount of acetone and dried in vacuo.

(xix) Preparation of $\underset{\sim}{5}$s ($R = \underline{o}$-Br, $A = I$, $Y = BF_4$)

This preparation was performed as in 3(i),
apart from the following:

(a) [Ir(CO)I(PPh$_3$)$_2$] was substituted for
     [Ir(CO)Cl(PPh$_3$)$_2$], $\underset{\sim}{1}$;

(b) $\underline{o}$-BrC$_6$H$_5$N$_2$BF$_4$ was substituted for C$_6$H$_5$N$_2$BF$_4$;

(c) the solid material obtained by freeze-drying the
     reaction solution was stirred in benzene (15 ml)
     for 2 hours, as in 3(i), and then filtered, providing
     a yellow-orange solid (A) and an orange-yellow
     filtrate (B). The filtrate (B) was kept at +10°C
     for 24 hours and the precipitated yellow crystals
     (25 mg) of product, $\underset{\sim}{5}$s, filtered-off, washed with
     cold (+5°C) benzene and dried in vacuo. The solid
     (A) was dissolved in the minimum volume of acetone
     ($\sim$2 ml). Benzene ($\sim$ 20 ml) was added to this
     solution, which was then kept at -5°C for 12 hours.
     The yellow crystalline product, $\underset{\sim}{5}$s (18 mg), which
     precipitated out was washed with cold benzene (+5°C)
     and dried in vacuo, and the filtrate was evaporated
     in vacuo until precipitation just started. This was
     then stored at -5°C until crystallisation appeared
     complete. The yellow crystals of $\underset{\sim}{5}$s (6 mg) were
     washed with cold benzene (+5°C) and dried in vacuo.

(xx) Preparation of $5t$ ($R = \underline{o}$-Br, $A = Br$, $Y = BF_4$)

This preparation was performed exactly as for 3(i),

substituting $[Ir(CO)Br(PPh_3)_2]$ for $[Ir(CO)Cl(PPh_3)_2]$, $\underline{1}$,

and $\underline{o}$-$BrC_6H_4N_2BF_4$ for $C_6H_5N_2BF_4$.

(xxi) Preparation of $5u$ ($R = \underline{o}$-Br, $A = OClO_3$, $Y = ClO_4$)

This preparation involved the synthesis of

$[Ir(CO)(OClO_3)(PPh_3)_2]$ from $[Ir(CO)Cl(PPh_3)_2]$ and $AgClO_4$

in benzene solution, and its reaction $\underline{in\ situ}$ with

$\underline{o}$-$BrC_6H_4N_2BF_4$ and ethanol:

$[Ir(CO)Cl(PPh_3)_2]$, $\underline{1}$ (0.25 mM, 195.2 mg) was dissolved, with

stirring, in benzene (30 ml). Anhydrous $AgClO_4$ (0.5 mM, 104 mg)

was added to this solution and stirring was continued, in the

dark, for 15 minutes. The resulting yellow-orange solution

was filtered to remove suspended AgCl. To the stirred filtrate

was added $\underline{o}$-$BrC_6H_4N_2BF_4$ (0.25 mM, 67.8 mg) and absolute

ethanol (10 ml), and stirring was continued, in the dark,

for 3 hours. The solution was filtered to remove suspended

$AgBF_4$, and the deep red-orange filtrate evaporated to dryness

by freeze-drying. The residual red and yellow solid mixture

was stirred in benzene (30 ml) for 2 hours, resulting, initially,

in complete dissolution followed by precipitation of the solid,

yellow product, $5u$. The product was recrystallised by dissol-

ving in acetone, adding diethyl ether until just cloudy, and

allowing to sit at room temperature until crystallisation was

complete. The crystals were filtered-off, washed with diethyl

ether containing a small volume of acetone, and dried $\underline{in\ vacuo}$.

4. Preparation of the molecular ortho-metalated arylazo complex [Ir(CO)Cl(PPh$_3$)$_2$(NNC$_6$H$_3$p-Br)], 6.

This preparation was effected by four different procedures (a, b, c, and d, below), all involving deprotonation of the aryldiimide complex, 5e, with a base. All of the procedures resulted in comparable yields of 6, procedure (a) being only slightly better than the others in this respect. It should be noted that where methanol is used as a solvent it can be satisfactorily substituted by ethanol.

Method a. [Ir(CO)Cl(PPh$_3$)$_2$(NHNC$_6$H$_3$p-Br)]BF$_4$, 5e (18 mg) was dissolved by stirring at room temperature in methanol (3 ml). To this yellow solution was added 1.0 ml of a solution of NaOH prepared by dissolving NaOH (32 mg) in water (10 ml) and methanol (10 ml). The yellow solution immediately turned pink, followed by precipitation of a pink solid. The solution-suspension was cooled to 0°C by surrounding with ice and was allowed to stir for a further 15 minutes. The pink solid product, 6, was filtered-off, washed several times with a total of 10 ml of a 50:50 mixture of methanol and water and dried in vacuo. The yield was 12 mg (73%).

Method b. This method was performed as in Method a, substituting 1.0 ml of a solution of CH$_3$COONa·3H$_2$O (90 mg) in water (10 ml) and methanol (10 ml) for the 1.0 ml of a solution of NaOH (32 mg) in water (10 ml) and methanol (10 ml). The yield of product, 6, was 11 mg (67%).

Method c. This method was performed as in Method a, substituting 2 drops ($\sim$0.04 ml) of triethylamine, Et_3N, and 1 ml of water for the 1.0 ml of a solution of NaOH (32 mg) in water (10 ml) and methanol (10 ml). The yield of product, 6, was 11.5 mg (70%).

Method d. [$Ir(CO)Cl(PPh_3)_2(NHNC_6H_3p-Br)$], 5e, (18 mg) was suspended in diethyl ether (5 ml). Two drops of Et_3N ($\sim$0.04 ml) were added to the stirred yellow suspension, and stirring was continued until the colour had apparently completely changed to pink. The pink solid product, 6, was filtered-off, washed with cold (0°C) diethyl ether and dried in vacuo. The yield was 11.5 mg (70%).

The arylazo complex, 6, prepared as described above in Methods a-d was reconverted to the aryldiimide complex 5e in greater than 70% yield by adding a 48% aqueous solution of HBF_4 dropwise to a stirred suspension of 6 in diethyl ether until the colour change from pink to yellow was apparently complete. The yellow product, 5e, was filtered-off, washed with diethyl ether and dried in vacuo.

5. Preparation of the cationic ortho-metalated arylhydrazine complexes [$Ir(CO)Cl(PPh_3)_2(NH_2NHC_6H_3R)$]$BF_4$, 7a-e

The complexes 7a (R = p-Br), 7b (R = o-Br), 7c (R = m-Br), 7d (R = o-Cl), and 7e (R = o-NH_2) were all prepared by the catalytic hydrogenation of the appropriate aryldiimide complexes 5e (R = p-Br), 5j (R = o-Br), 5n (R = m-Br), 5i (R = o-Cl) and 5k (R = o-NO_2), respectively. The procedure

was the same for all of the complexes 7a-d, as described below:

$[Ir(CO)Cl(PPh_3)_2(NH\ N\ C_6H_3R)]BF_4$, (20 mg) was dissolved, with stirring, in absolute ethanol (10 ml) under H_2 (one atmosphere) at room temperature. To this solution was added a 10% Pd on $BaSO_4$ catalyst (10 mg), and stirring was continued for 2 hours while a slow stream of H_2 was continuously bubbled through the solution (the reaction flask was fitted with a water-cooled reflux condenser to prevent loss of ethanol by evaporation). The mixture was centrifuged to remove the solid catalyst, and the ethanol solvent was completely evaporated off in vacuo. The residual solid (pale yellow for 7a-d, brownish-purple for 7e) was redissolved by stirring with benzene (10 ml). The resulting pale yellow solution was evaporated to dryness by freeze-drying, yielding the bulky, solid product, $[Ir(CO)Cl(PPh_3)_2(NH_2NHC_6H_3R)]BF_4$, 7a-e. The product was recrystallised from ethanol-diethyl ether, giving a yield of ~70-80%.

6. Preparation of the molecular ortho-metalated arylhydrazine complex $[Ir(CO)Cl(PPh_3)_2(NH_2NHC_6H_3p-Br)]\cdot(C_6H_5)_2O$, 9.

$[Ir(CO)Cl(PPh_3)_2(N=NC_6H_3p-Br)]$, 6 (20 mg) was stirred in absolute ethanol (10 ml) under H_2 (one atmosphere) at room temperature. To this pink solution-suspension was added a 10% Pd on $BaSO_4$ catalyst (10 mg), and stirring was continued for 2 hours while a slow stream of H_2 was

continuously bubbled through the solution (the reaction
flask was fitted with a water-cooled reflux condenser
to prevent loss of ethanol by evaporation). The resulting
red solution was centrifuged to remove suspended solid
catalyst, and the ethanol solvent was completely evaporated
off in vacuo. The residual pink-red solid was redissolved
in diethyl ether and filtered to remove a trace of insoluble
material. The filtrate was slowly evaporated in vacuo until
precipitation of the product, 9, resulted. The pink-red
solid product was filtered-off, washed with cold (-14°C)
diethyl ether and dried in vacuo.

7. Preparation of the molecular six-coordinate arylazo
   complexes (a) $[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$, 8a-f,[a] and
   (b) $[Ir(CO)Cl_2(PMe_2Ph)_2(NNC_6H_5)]$.

   (a) The complexes 8a (R = H), 8b (R = p-F), 8c (R = p-Br),
8d (R = p-OCH_3), 8e (R = o-F) and 8f (R = m-NO_2) were all
prepared by allowing $[Ir(CO)Cl(PPh_3)_2]$ (1), LiCl and the
appropriate aryldiazonium salt $(RC_6H_4N_2BF_4)$ to react
together in acetone solution   under an atmosphere of
argon, as described below for the general case,
$[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$:

   $[Ir(CO)Cl(PPh_3)_2]$, 1, (0.125 mM, 97.6 mg) was suspended
with stirring in acetone (10 ml). LiCl (0.125 mM, 6 mg)
and $RC_6H_4N_2BF_4$ (0.125 mM) were simultaneously added to this
suspension, and stirring under argon was continued for 1 hour.

a. See also Chapter VIII, B 12.

Initially, complete dissolution occurred and, generally, the product precipitated readily from solution at room temperature. Where precipitation did not occur after stirring for 1 hour, the reaction solution was cooled to +3°C when precipitation soon occurred (caution was required, as further cooling caused the co-precipitation of $LiBF_4$ and a solid having a low nitrogen content). The product,

$[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$, was filtered-off, washed with cold (-14°C) acetone and dried _in vacuo_. The colours and yields of the products, 8a-f, are recorded in Table VI-2.

(b) $[Ir(CO)Cl_2(PMe_2Ph)_2(NNC_6H_5)]$ was prepared according to the method of Deeming and Shaw:[144]

LiCl (13 mg) and $C_6H_5N_2BF_4$ (33 mg) were dissolved in methanol (2 ml) and water (1 ml). This solution was added to $[Ir(CO)Cl(PMe_2Ph)_2]$ (89 mg) under an atmosphere of argon, and the mixture was stirred for 30 minutes. The solid yellow-orange, fine crystalline product was filtered-off, washed with a 2:1 mixture of methanol:water, and dried _in vacuo_. The yield of product, $[Ir(CO)Cl_2(PMe_2Ph)_2(NNC_6H_5)]$, was 75 mg. The melting point (140-143°C), infrared and proton n.m.r. spectra agreed with those reported by Deeming and Shaw.[144]

8. Preparation of the cationic six-coordinate p-fluorophenyl-diimide complex $[Ir(CO)Cl_2(PPh_3)_2(NHNC_6H_4p-F)]BF_4$, 11: reaction of 8b with HBF_4.

$[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4p-F)]$, 8b (0.25 mM, 235 mg) was suspended with stirring in diethyl ether (10 ml) under an

atmosphere of argon. To this yellow suspension was added 48% aqueous HBF_4 (0.1 ml) and stirring continued for 1 hour. The suspension was filtered, and the resulting pale-yellow solid product, $[Ir(CO)Cl_2(PPh_3)_2(NHNC_6H_4p-F)]BF_4$, 11, washed with diethyl ether containing a small volume of ethanol and dried in vacuo. The yield of the product, 11, was 205 mg (80%).

The protonation of 8b to give 11 was readily reversed by treatment of a stirred suspension of 11 (20 mg) in diethyl ether (5 ml) with Et_3N (1 drop $\equiv$ ca. 0.02 ml) under an atmosphere of argon. The resulting yellow suspension was filtered, and the yellow solid product, 8b, washed with ethanol and dried in vacuo.

9. Reactions of the molecular six-coordinate arylazo complexes $[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$, 8, with $AgBF_4$ in (a) benzene and (b) benzene-ethanol.

(a) The complexes $[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$, 8b $(R = p-F)$, 8c $(R = p-Br)$, 8d $(R = p-OCH_3)$ and 8f $(R = m-NO_2)$ were all reacted with $AgBF_4$ in benzene medium as follows: $[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$, 8 $(3 \times 10^{-2} mM)$ was dissolved at room temperature by stirring with benzene (5 ml) under an atmosphere of argon. The reaction tube was protected from light by wrapping with aluminum foil. $AgBF_4$ $(3 \times 10^{-2} mM, 6 mg)$ was added to the yellow solution and stirring was continued for 15 minutes. The resulting suspension was centrifuged, yielding a white solid and a yellow solution. The benzene solvent was removed from the yellow solution by freeze-drying

leaving a yellow solid which was shown to be Vaska's complex, $\underset{\sim}{1}$, in high yield (but sometimes contaminated with a small amount of the starting complex, $\underset{\sim}{8}$). The white solid was stirred with acetone, resulting in a white insoluble solid (AgCl in 75-100% yield) and a solution. Diethyl ether was added to this solution, and the precipitated solid ($RC_6H_4N_2BF_4$ in 75-100% yield) isolated by centrifuging.

(b) The complexes $[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$, $\underset{\sim}{8b}$ (R = $\underline{p}$-F), $\underset{\sim}{8c}$ (R = $\underline{p}$-Br), $\underset{\sim}{8e}$ (R = $\underline{o}$-F) and $\underset{\sim}{8f}$ (R = $\underline{m}$-NO$_2$) were all reacted with $AgBF_4$ in benzene-ethanol medium as follows:

$[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4R)]$, $\underset{\sim}{8}$ (3×10^{-2}mM) was dissolved at room temperature by stirring with 9 ml of a 3:1 mixture of benzene:ethanol under an atmosphere of argon. The reaction tube was protected from light by wrapping with aluminum foil. $AgBF_4$ (3×10^{-2}mM, 6 mg) was added to the yellow solution and stirring was continued for 1 hour. The resulting suspension was centrifuged, yielding a white solid (AgCl in 80-100% yield) and a yellow ($\underset{\sim}{8e}$, $\underset{\sim}{8f}$) or an orange-red ($\underset{\sim}{8b}$, $\underset{\sim}{8c}$) solution; the orange-red colour was due to formation of the aryltetrazene complex, $\underset{\sim}{4}$, as confirmed at this stage by visible spectroscopy (c.f. Chapter II D4). The benzene solvent was removed from the (yellow or orange-red) solution by freeze-drying, and the aryldiimide complex was isolated from the residual solid by the appropriate method described in Chapter VIII B3, (ii) for $\underset{\sim}{8b}$, (v) for $\underset{\sim}{8c}$, (viii) for $\underset{\sim}{8e}$ and (xvi) for $\underset{\sim}{8f}$.

10. Preparation of the cationic five-coordinate arylazo

complexes $[Ir(CO)Cl(PPh_3)_2(NNC_6H_4R)]BF_4$, 2, where

(a) R = p-F and (b) R = o-F.

These complexes were prepared according to the methods

of N. Farrell.[172]

(a) R = p-F. $[Ir(CO)Cl(PPh_3)_2]$, 1, (0.25 mM, 195.2 mg)

and $p-FC_6H_4N_2BF_4$ (0.25 mM, 52.6 mg) were placed in a Schlenk

tube under an atmosphere of nitrogen at -25°C. To this was

added acetone (4 ml) at -25°C and the mixture was stirred,

maintaining the temperature at -25°C, until a clear orange

solution resulted. After a further 5 minutes stirring,

n-hexane (3.2 ml) at -25°C was slowly added and stirring

continued until a heavy, thick, yellow precipitate formed

within a few minutes. The precipitate was filtered-off under

nitrogen, washed with cold (-25°C) n-hexane and dried in vacuo,

being kept protected from light by wrapping the tube in

aluminum foil. This was shown from its melting point (116-

117°C), infrared spectrum and elemental analysis (required:

C-52.2%, H-3.5%, N-2.8%; found: C-51.5%, H-3.6%, N-2.7%)

to be $[Ir(CO)Cl(PPh_3)_2(NNC_6H_4p-F)]BF_4$. The yield of product

was 180 mg (72%).

(b) R = o-F. This method was performed as for the

p-fluoro complex (c.f. (a) above), except that when n-hexane

(3.2 ml) at -25°C was added to the acetone reaction solution at

-25°C, no precipitation of the product occurred, even after

stirring for 15 minutes. Further n-hexane (5 to 6 ml) at -25°C

was slowly added to the stirring solution until an oil formed. The two layers were allowed to separate, and the upper, light-yellow layer was removed (by pipette). The remaining oil was re-dissolved in acetone (4 ml) at -25°C. n-Hexane (5 to 6 ml) was added dropwise with rapid stirring at -25°C until a yellow solid precipitated from solution. After a further 5 minutes stirring at -25°C, the yellow product was filtered-off under nitrogen, washed with cold (-25°C) n-hexane and dried in vacuo, being kept protected from light by wrapping the tube in aluminum foil. The product was shown from its melting point (decomposed over 115-125°C), infrared spectrum and elemental analysis (required: C-52.2%, H-3.5%, N-2.8%; found: C-52.8%, H-3.7%, N-2.6%) to be [Ir(CO)Cl(PPh$_3$)$_2$(NNC$_6$H$_4$o-F)]BF$_4$. The yield of product was 74 mg (30%).

11. Decomposition of [Ir(CO)Cl(PPh$_3$)$_2$(NNC$_6$H$_4$p-F)]BF$_4$
    in benzene.

   [Ir(CO)Cl(PPh$_3$)$_2$(NNC$_6$H$_4$p-F)]BF$_4$ (40 mg) was stirred with benzene (10 ml) at room temperature for 3 minutes under an atmosphere of nitrogen. The white insoluble solid which formed was filtered-off, washed with benzene, and dried in vacuo. This was shown by its infrared spectrum to be p-FC$_6$H$_4$N$_2$BF$_4$ in 75% yield (6 mg). The yellow benzene filtrate was evaporated to dryness by freeze-drying, leaving a yellow solid (31 mg) shown by its infrared spectrum to be slightly impure Vaska's complex, [Ir(CO)Cl(PPh$_3$)$_2$], 1.

12. Reaction of $[Ir(CO)Cl(PPh_3)_2(NNC_6H_4\underline{o}-F)]BF_4$ with LiCl in acetone.

This reaction provides an alternative synthetic route to the molecular six-coordinate arylazo complexes, $\underset{\sim}{8}$ (c.f. Chapter VIB and Chapter VIIIB7).

$[Ir(CO)Cl(PPh_3)_2(NNC_6H_4\underline{o}-F)]BF_4$ (26 mg) was placed in a Schlenk tube under an atmosphere of argon and was cooled to $-25°C$. To this was added 0.05 M LiCl (2 ml) in acetone with stirring at $-25°C$. Dissolution occurred immediately, quickly followed by precipitation of an orange solid. Stirring was continued for 15-minutes, and the orange solid was then filtered-off, washed with cold acetone (some dissolution of the product occurred) and dried in vacuo. The infrared spectrum of this orange product was identical to that for the cationic six-coordinate arylazo complex $\underset{\sim}{8}$e,

$[Ir(CO)Cl_2(PPh_3)_2(NNC_6H_4\underline{o}-F)]$.

13. Determination of acetone produced in the reaction between $[Ir(CO)Cl(PPh_3)_2]$, $\underset{\sim}{1}$ and $\underline{p}$-BrC$_6$H$_4$N$_2$BF$_4$ in benzene-iso-propanol (3:1).

$[Ir(CO)Cl(PPh_3)_2]$, $\underset{\sim}{1}$ (0.125 mM, 97.6 mg) and $\underline{p}$-BrC$_6$H$_4$N$_2$BF$_4$ (0.125 mM, 33.8 mg) were placed in a 100 ml flask (flask A) which was then attached to a vacuum line and thoroughly degassed. A degassed mixture of acetone-free benzene (15 ml) and acetone-free iso-propanol (5 ml) was distilled under vacuum into flask A, which had been cooled

to liquid nitrogen temperature. Flask A was sealed with a
flame and the frozen mixture allowed to come to room temperature
and then stirred for 3 hours. The resulting orange-red
solution in flask A was again attached to the vacuum line,
frozen by immersing in liquid nitrogen, and then opened,
under vacuum, to a tube (tube B) also cooled in liquid
nitrogen. The solution in flask A was allowed to come to
room temperature and the solvent was completely and
quantitatively distilled into tube B. The 20 ml of solvent
thus collected was quantitatively analyzed for acetone content
by the gas chromatography of 1.5 μl on a 10% 20M carbowax
column (6' x 1/8") at 30°C, using a Varian Aerograph 1400
gas chromatograph instrument. The measured area of the
observed peak due to acetone was compared with the areas,
obtained by the gas chromatography, under the same conditions,
of 1.5 μl aliquots of standard solutions containing 4 to 10 μl
of acetone in 20 ml of solvent (15 ml acetone-free benzene
plus 5 ml acetone-free iso-propanol).

The benzene and iso-propanol solvents used in the above
procedure were purified by fractionation on a spinning-band
column, and were then carefully checked for the absence of
acetone and interfering low-boiling components by gas
chromatography under exactly the same conditions as described
above.

14. Effect of added phenyldiazene, $C_6H_5N=NH$, on the

formation of $[Ir(CO)(PPh_3)_2\{N_4(C_6H_5)_2\}]BF_4$, $\underset{\sim}{4a}$:

reaction between $[Ir(CO)Cl(PPh_3)_2]$, $\underset{\sim}{1}$ and $C_6H_5N_2BF_4$

in the presence of $C_6H_5N=NH$ in benzene-ethanol medium

This procedure involved three separate reactions, (i),

(ii) and (iii) as indicated by Equations VIII-1, VIII-2

and VIII-3, respectively:

(i) $nCuCl_2 + C_6H_5NHNH_2 \xrightarrow{H_2O} (C_6H_5N=NH)Cu_nCl_n$ (VIII-1)
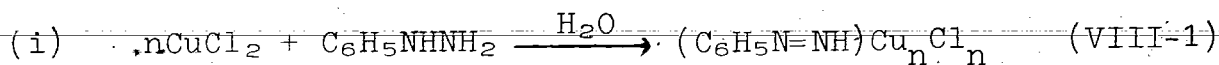
As there is some dubiety in the literature[161,163]

as to whether n=2 or 4 (Equation VIII-1), it was decided

in this work to take n=4.

(ii) $(C_6H_5N=NH)Cu_nCl_n + 2nbipy \longrightarrow nCu(bipy)_2^+ + (C_6H_5N=NH)$

(VIII-2)

(iii) $[Ir(CO)Cl(PPh_3)_2] + C_6H_5N_2BF_4 \xrightarrow[C_6H_5-EtOH]{[C_6H_5N=NH]}$

$[Ir(CO)(PPh_3)_2\{N_4(C_6H_5)_2\}]BF_4$ (VIII-3)
$\underset{\sim}{4a}$
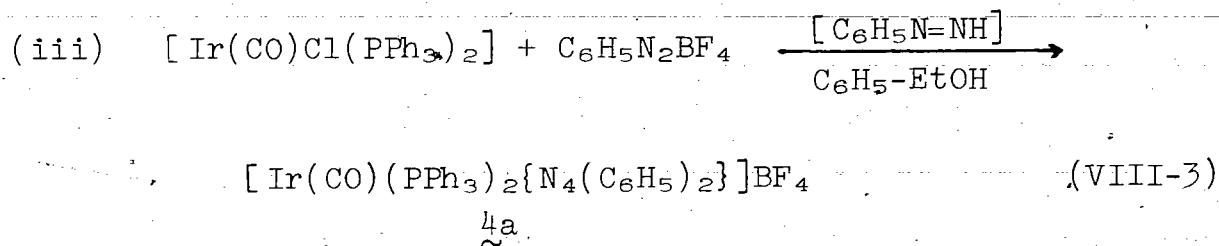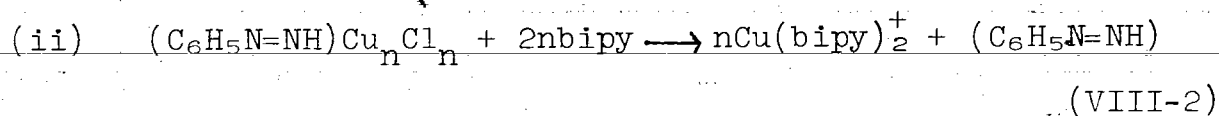
In view of the highly reactive nature of $C_6H_5N=NH$,

and in particular its propensity to undergo oxidation and

bimolecular disappearance,[159-161] oxygen must be excluded

and dilute solutions ($\not> 10^{-4}M$) must be used in its generation.

The reactions (ii) and (iii) were performed under vacuum in

the glass apparatus illustrated in Figure VIII-1.

Reaction (i), preparation of $(C_6H_5N=NH)Cu_nCl_n$:
$CuCl_2 \cdot 2H_2O$ (8 mM, 1.364 g) was dissolved in water (20 ml)
and the solution was filtered to remove the small amount
of insoluble material. The clear, blue filtrate was
deoxygenated by bubbling argon through the solution, and
to this was added $C_6H_5NHNH_2$ (2 mM, 0.216 g). The mixture
was stirred vigorously under an atmosphere of argon until
precipitation of the brown, solid product appeared complete.
The brown solid was filtered-off under argon and washed
thoroughly, first with water and then with absolute ethanol
and dried in vacuo. The infrared spectrum (KBr disc) of
the product agreed with that reported by Petredis et al[163]
for $(C_6H_5N=NH)Cu_nCl_n$.

Reactions (ii), generation of $C_6H_5N=NH$ and (iii),
reaction of $[Ir(CO)Cl(PPh_3)_2]$, 1, and $C_6H_5N_2BF_4$ in the
presence of $C_6H_5N=NH$: Bipyridyl (0.8 mM, 125 mg) was
placed in side-arm a of the apparatus (Figure VIII-1), and
$(C_6H_5N=NH)Cu_nCl_n$ (0.1 mM, 50.2 mg), ethanol (5 ml) and
a stirrer-bar in flask b. Side-arm a was sealed-off, and
flask b was attached to the vacuum line and degassed
through three freeze-thaw cycles with liquid nitrogen as
coolant. Flask b was sealed-off. $[Ir(CO)Cl(PPh_3)_2]$, 1,
(0.1 mM, 78 mg), $C_6H_5N_2BF_4$ (0.1 mM, 19.2 mg), benzene (15 ml)
and a stirrer-bar were added to flask c cooled in liquid nitrogen.
Flask c was thoroughly degassed on the vacuum line and then
sealed-off. While flask c was kept at liquid nitrogen temperature,

the bipyridyl in <u>a</u> was added to the stirred contents of
flask <u>b</u> at room temperature and the break-seal between
<u>b</u> and <u>c</u> was broken. When distillation of the ethanolic
phenyldiazene solution from <u>b</u> to <u>c</u> was complete, the
contents of <u>c</u> were allowed to come to room temperature and
then stirred for one hour. The visible spectrum of the
resulting orange-red solution was determined and the yield
of phenyltetrazene complex $[Ir(CO)(PPh_3)_2\{N_4(C_6H_5)_2\}]BF_4$,
<u>4a</u>, calculated from the molar absorptivity, ϵ_{500nm} (c.f.
Table 11-7).
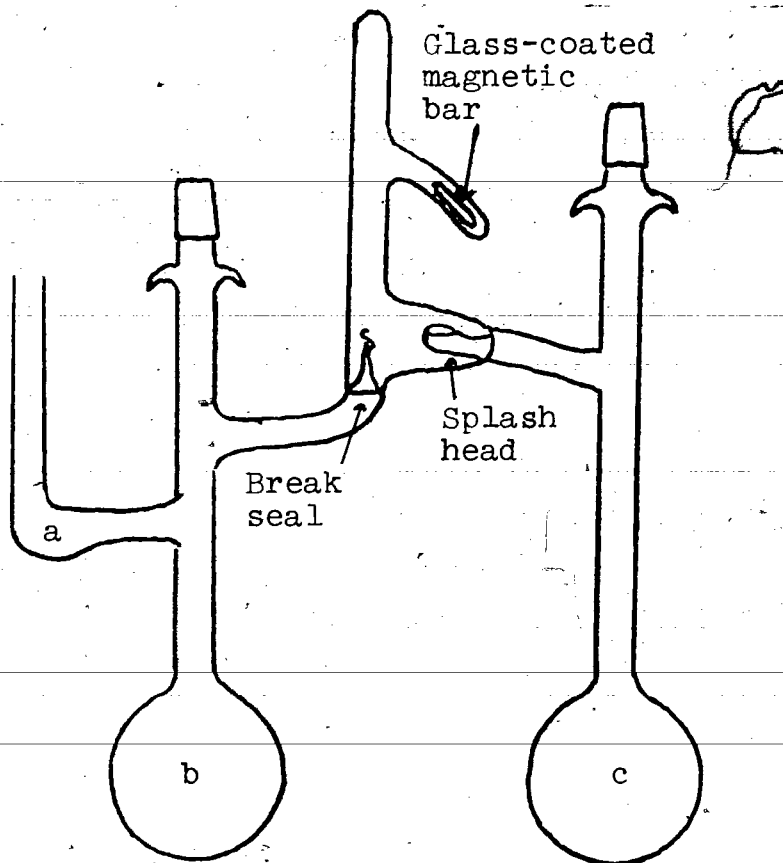
Figure VIII-1

15. Reaction between $[Ir(CO)Cl(PPh_3)_2(HNNC_6H_3p-Br)]BF_4$, $\underset{\sim}{5}e$, and D_2 gas.

$[Ir(CO)Cl(PPh_3)_2(HNNC_6H_3p-Br)]BF_4$, $\underset{\sim}{5}e$ (25 mg) was dissolved, with stirring, in ethanol (10 ml) under an atmosphere of argon at room temperature (31°C); the reaction flask was fitted with a water-cooled reflux condenser to prevent loss of solvent by evaporation. Argon was first bubbled through the yellow solution for 15 minutes, and then deuterium gas for 6 hours at room temperature. The solvent was completely removed, _in vacuo_, from the resulting yellow solution, and the residual yellow, solid product washed with diethyl ether and dried _in vacuo_. This yellow, solid product was re-dissolved in 5 ml of methanol-d¹ (CH_3OD), reacted with deuterium gas for a further 6 hours, and the yellow, solid product isolated exactly as described above for the ethanol case.

Appendix

A.   Definitions and Methods of Calculation of the
    Electronegativities (X_A), Total Electronegativities
        (X_T) and π-Electronegativities (X_π) of the
            Anionic Ligands, A, in the Complexes
                $[Ir(CO)(A)(PPh_3)_2]$ (1, 1a-d) and
        $[Ir(CO)A(PPh_3)_2(HN=NC_6H_3O-Br)]Y$ (5j, r-u)
                as listed in Table III-7.

Definitions[42]

X_A = "sigma" electronegativity of the anionic ligand, A

   (by which A withdraws charge from the metal by

   purely inductive effects).

X_π = π-electronegativity of the anionic ligand, A (by

   which A can accept charge into empty low-lying d-

   orbitals or π^* molecular orbitals.

X_T = total electronegativity of the anionic ligand A:

   $$X_T = X_A + X_\pi \tag{1}$$

Methods of Calculation[42]

   The following basic assumptions are made:

(i)   the fluoro-ligand is not involved in back acceptance of

   π-electron density from the metal, so that $X_\pi = 0$

(ii)   in the bonding between Ir and A, and Ir and CO a com-

   pletely synergistic mechanism is operative, such that

   the total electronegativity (consisting of σ- and π-

components) of A is inversely related to the change in the force constant, k_{CO}, of the carbon-oxygen bond of the coordinated carbonyl group (as compared to k_{CO} of free CO).

i.e., $X_T \propto \dfrac{1}{\Delta k_{CO}}$ (2)

since $k_{CO} \propto \nu^2_{CO}$ (3)

then $X_T \propto \dfrac{1}{\Delta \nu^2_{CO}}$ (4)

and $X_T \Delta \nu^2_{CO} = $ constant (5)

where $\Delta \nu^2_{CO} = \nu^2_{CO}$ of gaseous $CO - \nu^2_{CO}$ of coordinated CO.

Since, by definition, $X_\pi = 0$, then $X_T = X_A = 4.02$. This value is calculated from the Willmhurst equation[154], which is

$$X_A = \left[1.104 \times 10^{-3} \left(1 + \dfrac{M_H}{M_A} \right)^{-\frac{1}{2}} (\nu_{HA}) \right] - 0.24 \qquad (6)$$

where $M_H = $ mass of hydrogen

$M_A = $ mass of group bonded to hydrogen in an H-A compound

$\nu_{HA} = $ stretching frequency for the H-A molecule.

Application of Equation (5) gives

$$(X_T \Delta \nu^2_{CO})_F = (X_T \Delta \nu^2_{CO})_A \qquad (7)$$

Equation (7) allows calculation of the total electronegativity, X_T (with ν_{CO} of free CO = 2143 cm^{-1} and X_T of F defined as 4.02);

for the anionic ligand, A. The π-electronegativity, X_π, is calculated from Equation (1).
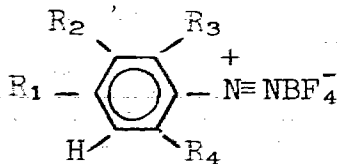
B. Accurate ($\pm 1 cm^{-1}$) Infrared Stretching Frequencies, $\nu^+_{N\equiv N}$, for some Aryldiazonium Salts, ArN_2BF_4.

The $\nu^+_{N\equiv N}$ values for the aryldiazonium salts are listed in Table B1 and were determined to an accuracy of $\pm 1 cm^{-1}$ using a Beckman IR12 Spectrometer calibrated against DCl gas. In all cases, spectra were obtained on samples pressed in KBr.

Table B-1

Infrared stretching frequencies, $\nu_{N\equiv N}^{+}$, for

some aryldiazonium tetrafluoroborates,

R_1	R_2	R_3	R_4	$\nu_{N\equiv N}^{+}$ $(\pm 1\text{cm}^{-1})$[a,b]
F	H	H	H	2297
Cl	H	H	H	2295
Br	H	H	H	2291
NO$_2$	H	H	H	2308
CF$_3$	H	H	H	2310
H	H	H	H	2298
CH$_3$	H	H	H	2291
OCH$_3$	H	H	H	2257
OH	H	H	H	2250
NEt$_2$	H	H	H	2155
H	F	H	H	2295
H	Cl	H	H	2311
H	Br	H	H	2309
H	NO$_2$	H	H	2308
H	CH$_3$	H	H	2302
H	OCH$_3$	H	H	2306
H	H	F	H	2300
H	H	Cl	H	2295
H	H	Br	H	2293
H	H	NO$_2$	H	2297
H	H	CH$_3$	H	2288
H	H	OCH$_3$	H	2277
H	H	Cl	Cl	2292
Br	H	Cl	I	2266

a. KBr pellet

b. Values for comparative purposes can be found in references 175-179.

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