National Library of Canada
Bibliothèque nationale du Canada

Acquisitions and Bibliographic Services Branch
Direction des acquisitions et des services bibliographiques

395 Wellington Street
Ottawa, Ontario
K1A 0N4

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

SYNTHESES OF IRIDIUM COMPLEXES WITH DOUBLY BENT ARYLDIAZENIDO LIGANDS

by

Grace Chi-Young Kim

B.Sc., University of British Columbia, 1992

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
in the Department
of
Chemistry

© Grace Chi-Young Kim 1995

Simon Fraser University

February 1995

All right reserved. This thesis may not be
reproduced in whole or in part, by photocopy
or other means, without permission of the author.

National Library of Canada
Bibliothèque nationale du Canada

Acquisitions and Bibliographic Services Branch
Direction des acquisitions et des services bibliographiques

395 Wellington Street
Ottawa, Ontario
K1A 0N4

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

THE AUTHOR HAS GRANTED AN IRREVOCABLE NON-EXCLUSIVE LICENCE ALLOWING THE NATIONAL LIBRARY OF CANADA TO REPRODUCE, LOAN, DISTRIBUTE OR SELL COPIES OF HIS/HER THESIS BY ANY MEANS AND IN ANY FORM OR FORMAT, MAKING THIS THESIS AVAILABLE TO INTERESTED PERSONS.

L'AUTEUR A ACCORDE UNE LICENCE IRREVOCABLE ET NON EXCLUSIVE PERMETTANT A LA BIBLIOTHEQUE NATIONALE DU CANADA DE REPRODUIRE, PRETER, DISTRIBUER OU VENDRE DES COPIES DE SA THESE DE QUELQUE MANIERE ET SOUS QUELQUE FORME QUE CE SOIT POUR METTRE DES EXEMPLAIRES DE CETTE THESE A LA DISPOSITION DES PERSONNE INTERESSEES.

THE AUTHOR RETAINS OWNERSHIP OF THE COPYRIGHT IN HIS/HER THESIS. NEITHER THE THESIS NOR SUBSTANTIAL EXTRACTS FROM IT MAY BE PRINTED OR OTHERWISE REPRODUCED WITHOUT HIS/HER PERMISSION.

L'AUTEUR CONSERVE LA PROPRIETE DU DROIT D'AUTEUR QUI PROTEGE SA THESE. NI LA THESE NI DES EXTRAITS SUBSTANTIELS DE CELLE-CI NE DOIVENT ETRE IMPRIMES OU AUTREMENT REPRODUITS SANS SON AUTORISATION.

ISBN 0-612-06694-0

Canada

APPROVAL

Name: Grace Chi-Young Kim

Degree: Master of Science

Title of Thesis: Syntheses of Iridium Complexes with Doubly Bent Aryldiazenido Ligands.

Examining Committee:

Chair: Dr. S. Holdcroft (Associate Professor)

Dr. D. Sutton (Professor)
Senior Supervisor

Dr. L. K. Peterson (Associate Professor)
Committee Member

Dr. K. N. Slessor (Professor)
Committee Member

Dr. G. Leach (Assistant Professor)
Internal Examiner

Date Approved: 6 Feb '95

PARTIAL COPYRIGHT LICENSE

I hereby grant to Simon Fraser University the right to lend my thesis, project or extended essay (the title of which is shown below) to users of the Simon Fraser University Library, and to make partial or single copies only for such users or in response to a request from the library of any other university, or other educational institution, on its own behalf or for one of its users. I further agree that permission for multiple copying of this work for scholarly purposes may be granted by me or the Dean of Graduate Studies. It is understood that copying or publication of this work for financial gain shall not be allowed without my written permission.

Title of Thesis/Project/Extended Essay:

Syntheses of Iridium Complexes with Doubly Bent Aryldiazenido ligands

Author:

(signature)

Grace Chi-Young Kim

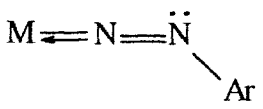
(name)

Feb 7, 95

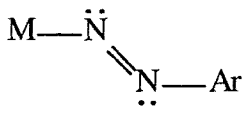
(date)

ABSTRACT

In mononuclear aryldiazenido compounds, the N_2Ar (Ar = p-C_6H_4OMe) group may adopt a "singly bent" (I) or a "doubly bent" (II) coordination mode depending on the metal environment.



SINGLY BENT
(I)



DOUBLY BENT
(II)

In contrast to a large number of singly bent aryldiazenido complexes isolated to date, only a few doubly bent aryldiazenido complexes are known. This thesis reports several new doubly bent aryldiazenido complexes that are formed by systematically converting the singly bent aryldiazenido ligand in the complex into the doubly bent aryldiazenido ligand. This synthetic route had not been explored in detail in the past.

The new compounds have been characterized by ^{1}H, ^{31}P, and ^{15}N NMR spectroscopy, elemental analyses, and by a crystal structure determination. The ^{15}N NMR spectroscopy was utilized to unambiguously characterize the aryldiazenido coordination mode in the newly synthesized iridium complexes, since there is a dramatic difference in $^{15}N_{\alpha}$ resonances between a singly bent (100 to –47 ppm) and a doubly bent (290 to 200 ppm) aryldiazenido ligands.

New doubly bent aryldiazenido complexes of general formula $[Cp^*Ir(PPh_3)(L)(N_2Ar)]^{+,0}$ (L = PMe_3, CO, CN^-) were synthesized by introducing a quantitative amount of L to the stable singly bent aryldiazenido complex $[Cp^*Ir(PPh_3)(N_2Ar)][BF_4]$. The doubly bent aryldiazenido complex $[Cp^*Ir(diphos)(N_2Ar)][BF_4]$ was also synthesized in an attempt to shed some light on the

unsuccessful attempt to isolate the complex $[Cp^*Ir(PPh_3)_2(N_2Ar)][BF_4]$, which is perhaps sterically unfavoured .

A new singly bent aryldiazenido complex $[Cp^*Ir\{P(p\text{-tol})_3\}(N_2Ar)][BF_4]$ (1) was isolated and further reacted with PMe_3 to yield a new doubly bent aryldiazenido complex $[Cp^*Ir\{P(p\text{-tol})_3\}(PMe_3)(N_2Ar)][BF_4]$. The X-ray crystal structure of (1) was determined by Drs. R. J. Batchelor and F. W. B. Einstein and was found to have $\angle$ Ir-N(1)-N(2) = 177.7(6)°; $\angle$N(1)-N(2)-C = 120.2(7)°; Ir-N(1) = 1.811(6) Å; N(1)-N(2) = 1.205(8) Å, which are in the expected range for singly bent aryldiazenido complexes.

Another new doubly bent aryldiazenido complex $[Cp^*Ir(PMe_3)_2(N_2Ar)][BF_4]$ (2) was synthesized by introducing an excess amount of PMe_3 to $[Cp^*Ir(C_2H_4)(N_2Ar)][BF_4]$. The X-ray crystal structure of (2) was also determined and it clearly demonstrates its doubly bent N_2Ar coordination mode ($\angle$ Ir-N(1)-N(2) = 123.9(6)°; $\angle$ N(1)-N(2)-C = 117.1(8)°; Ir-N(1) = 2.028(7) Å; N(1)-N(2) = 1.210(10) Å). This is only the fourth structurally determined example of a doubly bent aryldiazenido complex to date.

To my parents

ACKNOWLEDGMENTS

I would first like to express my sincere gratitude to my senior supervisor, Dr. Derek Sutton, for his helpful advice, supervision and assistance.

I gratefully acknowledge Drs. R. J. Batchelor and F. W. B. Einstein for the X-ray crystal structure determinations, Ms. M. M. Tracey for the ^{31}P and ^{15}N NMR spectra, Mr. G. L. Owen for the mass spectra, and Mr. M. K. Yang for the elemental analyses.

I would also like to thank my labmates and colleagues who provided me with continued support and knowledge during my time spent at Simon Fraser University. In particular, I sincerely thank Dr. Xiaoqian Yan for his guidance and enthusiasm.

I am also grateful to Drs. R. K. Pomeroy and R. H. Hill for the quality instructions they provided to me.

Finally, I truly thank my family and very special friend for their unconditional support and encouragement ... *it meant so much to me*.

TABLE OF CONTENTS

Approval page		ii
Abstract		iii
Dedication		v
Acknowledgements		vi
Table of Contents		vii
List of Tables		x
List of Figures		xi
List of Compounds		xii
Nomenclature and Structure		xiii
List of Abbreviations and Symbols		xiv
CHAPTER I	INTRODUCTION	1
1.1	General background	1
1.2	Research project	9
1.2.1	Background	9
1.2.2	Research outline	10
1.3	Important techniques	12
1.3.1	X-ray crystallography	12
1.3.2	Infrared spectroscopy	13
1.3.3	^{15}N NMR spectroscopy	14
CHAPTER II	RESULTS	16
2.1	Preparation of the starting materials	16
2.2	Synthesis and characterization of singly bent aryldiazenido compound $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1)	16

2.3	Syntheses and characterization of doubly bent aryldiazenido compounds of type $[(\eta^5\text{-}C_5Me_5)Ir(L_1)(L_2)(p\text{-}N_2C_6H_4OMe)][BF_4]$	24
2.3.1	$[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2)	25
2.3.2	$[Cp^*Ir(PPh_3)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (3) and $[Cp^*Ir\{P(p\text{-tol})_3\}(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$(4)	26
2.3.3	$[Cp^*Ir(diphos)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (5)	31
2.3.4	$[Cp^*Ir(PPh_3)(CO)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (6) and $[Cp^*Ir(PPh_3)(CN)(p\text{-}N_2C_6H_4OMe)]$ (7)	31
2.3.5	X-ray structure of $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1)	32
2.3.6	X-ray structure of $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2)	33
CHAPTER III	DISCUSSION	39
3.1	Historical background	39
3.2	Synthetic route	41
3.3	New doubly bent aryldiazenido compounds	42
3.3.1	Iridium singly bent aryldiazenido precursor	43
3.3.2	Systematic isolation of iridium doubly bent aryldiazenido compounds	45
3.3.3	Other co-ligands which favour singly bent - doubly bent N_2Ar conversion	47
3.4	X-ray crystal structures	48
3.5	Conclusion	53
CHAPTER IV	EXPERIMENTAL	54
4.1	General procedures	54
4.2	Syntheses	55
4.2.1	Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C**	55

4.2.2 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1) 55

4.2.3 Reaction of $P(p\text{-tol})_3$ with $[p\text{-}N_2C_6H_4OMe][BF_4]$ 56

4.2.4 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2) 56

4.2.5 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (3) 57

4.2.6 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir\{P(p\text{-tol})_3\}(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (4) 57

4.2.7 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(Ph_2PC_2H_4PPh_2)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (5) 58

4.2.8 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(CO)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (6) 58

4.2.9 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(CN)(p\text{-}N_2C_6H_4OMe)]$ (7) 59

REFERENCES 60

LIST OF TABLES

Table		Page
1.1	Characterization of Doubly Bent Aryldiazenido Complexes	7
1.2	Characterization of Doubly Bent Aryldiazenido Complexes	8
2	Electronic and Steric Parameters of Selected Phosphorus Ligands	11
3	Structural data for Selected Aryldiazenido Complexes	13
4	NN Stretching Frequencies and ^{15}N Chemical Shift Data for Selected Aryldiazenido Complexes	14
5	Summary of ^{1}H (100 MHz), ^{15}N (40.5 MHz) and $^{31}P\{^{1}H\}$ (162 MHz) NMR Data	23
6	Selected Distances, Angles and Torsion Angles for $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)]^+$	36
7	Selected Distances, Angles and Torsion Angles for $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$	38
8	Selected Bond Distances(Å) and Angles(°) for Iridium Singly Bent Aryldiazenido complexes	49
9	Selected Bond Distances(Å) and Angles(°) for Doubly Bent Aryldiazenido Complexes	52

LIST OF FIGURES

Figure		Page
1	Proposed synthesis of doubly bent aryldiazenido complexes	10
2	Synthetic scheme for starting complexes	17
3	Synthesis of $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1)	18
4	IR spectrum of $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1) in ethanol	20
5	100 MHz ^1H NMR spectrum of $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1) in acetone-d_6	21
6	162 MHz $^{31}P\{^1H\}$ and 40.5 MHz ^{15}N NMR spectra of $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1)	22
7	Syntheses of doubly bent aryldiazenido compounds	24
8	100 MHz ^1H NMR spectrum of $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2) in acetone-d_6	27
9	162 MHz $^{31}P\{^1H\}$ and 40.5 MHz ^{15}N NMR spectra of $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2)	28
10	162 MHz $^{31}P\{^1H\}$ NMR spectrum of $[Cp^*Ir(PPh_3)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (3)	29
11	162 MHz $^{31}P\{^1H\}$ NMR spectrum of $[Cp^*Ir\{P(p\text{-tol})_3\}(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (4)	30
12	Perspective view of the cation $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)]^+$	35
13	Perspective view of the cation $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$	37
14	(a) $\pi \leftrightarrow \pi^*$ and (b) $n \leftrightarrow \pi^*$ transitions at the N_2Ar group	44
15	N_2Ar ligand orientation in (a) $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)]^+$ and (b) $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$	50
16	Molecular structures of doubly bent aryldiazenido compounds	51

LIST OF COMPOUNDS

(1) $[(\eta^5\text{-}C_5Me_5)Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$

(2) $[(\eta^5\text{-}C_5Me_5)Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$

(3) $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$

(4) $[(\eta^5\text{-}C_5Me_5)Ir\{P(p\text{-tol})_3\}(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$

(5) $[(\eta^5\text{-}C_5Me_5)Ir(Ph_2PC_2H_4PPh_2)(p\text{-}N_2C_6H_4OMe)][BF_4]$

(6) $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(CO)(p\text{-}N_2C_6H_4OMe)][BF_4]$

(7) $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(CN)(p\text{-}N_2C_6H_4OMe)]$

A $[(\eta^5\text{-}C_5Me_5)Ir(C_2H_4)_2]$

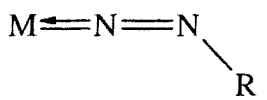
B $[(\eta^5\text{-}C_5Me_5)Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$

C $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$

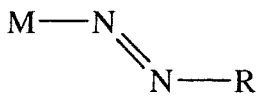
D $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)H(p\text{-}N_2C_6H_4OMe)]$

E $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)Cl(p\text{-}NHNC_6H_4OMe)][BF_4]$

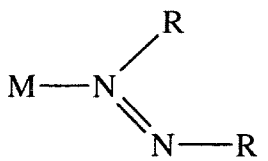
NOMENCLATURE AND STRUCTURE



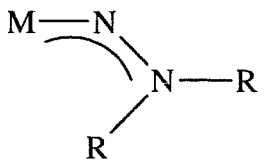
Singly Bent Diazenido



Doubly Bent Diazenido



Diazene



Hydrazido (2–)

LIST OF ABBREVIATIONS AND SYMBOLS

Å	=	Angstrom unit 10^{-8} cm
Ar	=	aryl
cm^{-1}	=	wavenumber
Cp*	=	η^5 - pentamethylcyclopentadienyl, η^5-$C_5(CH_3)_5$
d	=	doublet
δ	=	chemical shift
diphos	=	bis(diphenylphosphino)ethane, $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$
dtc	=	dimethyldithiocarbamate, $S_2CN(CH_3)_2$
EI	=	electron impact
Et	=	ethyl, C_2H_5
EtOH	=	ethanol, C_2H_5OH
FAB	=	fast atom bombardment
FT	=	Fourier transform
HOMO	=	highest occupied molecular orbital
Hz	=	Hertz, sec^{-1}
IR	=	infrared
L	=	unidentate ligand
LUMO	=	lowest unoccupied molecular orbital
m	=	multiplet
M	=	central transition metal
Me	=	methyl, CH_3
MS	=	mass spectroscopy
ν	=	frequency in cm^{-1}
NMR	=	nuclear magnetic resonance
NOBA	=	*m*-nitrobenzyl alcohol, *m*-$O_2NC_6H_4CH_2OH$

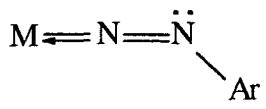
OMe	=	methoxy, OCH_3
Ph	=	phenyl, C_6H_5
PMe_3	=	trimethylphosphine, $P(CH_3)_3$
PMe_2Ph	=	dimethylphenylphosphine, $P(CH_3)_2(C_6H_5)$
PPh_3	=	triphenylphosphine, $P(C_6H_5)_3$
ppm	=	parts per million
PPP	=	{bis(1-diphenylphosphinopropyl)}phenylphosphine $C_6H_5P\{(CH_2)_3P(C_6H_5)_2\}_2$
$P(p\text{-tol})_3$	=	tri- *p*-tolylphosphine, $P(p\text{-}C_6H_4CH_3)_3$
s	=	singlet
t	=	triplet
THF	=	tetrahydrofuran
TMS	=	tetramethylsilane, $Si(CH_3)_4$

SYNTHESES OF IRIDIUM COMPLEXES WITH DOUBLY BENT ARYLDIAZENIDO LIGANDS

CHAPTER I INTRODUCTION

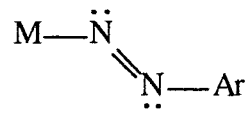
1.1 GENERAL BACKGROUND

Over the last two decades, there has been a great interest in the study of the aryldiazenido ligand (NNAr) in transition metal compounds with respect to its capability of adopting a wide range of coordination geometries.[1] In mononuclear aryldiazenido compounds, the N_2Ar ligand can bind to the metal in three different coordination modes depending on the ancillary ligands in the system.[1,2,3] They are singly bent (I), doubly bent (II), and side-on (III) geometries.



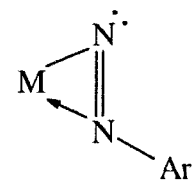
SINGLY BENT

(I)



DOUBLY BENT

(II)



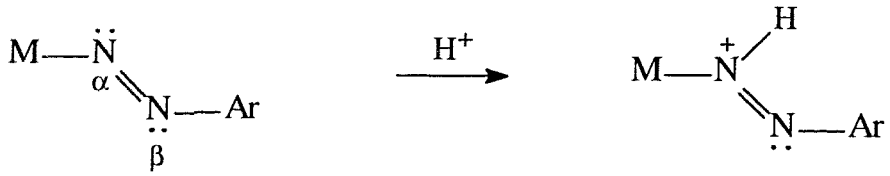
SIDE-ON

(III)

Different bonding modes of the aryldiazenido ligand directly reflect the different electronic configurations and the charge density distributions within the M-NNAr linkages. In the singly bent case (I), the aryldiazenido ligand can be viewed as a three electron donor terminal radical or a two electron donor cation (N_2Ar^+). The doubly bent aryldiazenido ligand (II), on the other hand, can be viewed as either a one electron donor radical or a two electron donor anionic (N_2Ar^-) ligand. Finally, the side-on aryldiazenido ligand (III) donates three electrons in total to the metal center, but from both nitrogens.

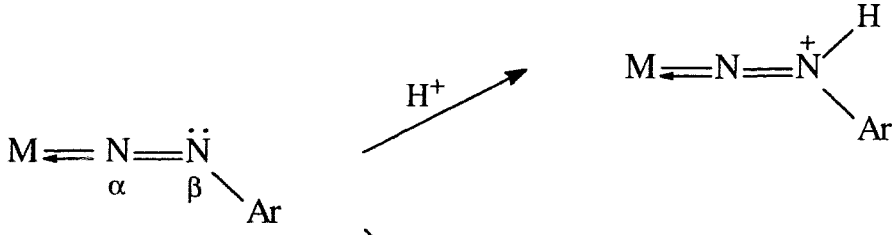
Furthermore, these coordination modes, in turn, can be correlated to the various reaction chemistry exhibited by the aryldiazenido complexes. According to previous studies on protonation or alkylation of an organodiazenido ligand, electrophilic attack can occur at

N_α or N_β depending on its geometry. For example, doubly bent N_2Ar ligands always seem to protonate at the more basic nitrogen N_α, forming an organodiazene ligand (Eq. 1). Some supporting examples include $[PtCl(PEt_3)_2(N_2Ph)]$[4], $[IrCl_2(CO)(PPh_3)_2(N_2Ph)]$[5], and $[RuCl(CO)_2(PPh_3)_2(N_2Ph)]$.[6]

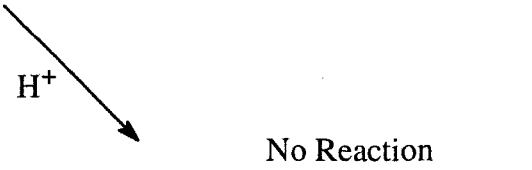


(Eq. 1)

In contrast, singly bent N_2Ar ligands protonate (or alkylate) either at the more basic nitrogen $N\beta$ (Eq. 2) (due to the lone pair), or do not protonate at all (Eq. 3), depending on the metal environment. For example, $[ReCl_2(NH_3)(PMe_2Ph)(N_2Ph)]$[7,8] and $[Mo(dtc)_3(p\text{-}N_2C_6H_4R)]$[9] protonate at $N\beta$, while $[ReCl_2(CO)(PMe_2Ph)(N_2Ph)]$[7,8] and $[OsCl_3(PPh_3)_2(N_2Ph)]$[6] do not protonate at either nitrogen.



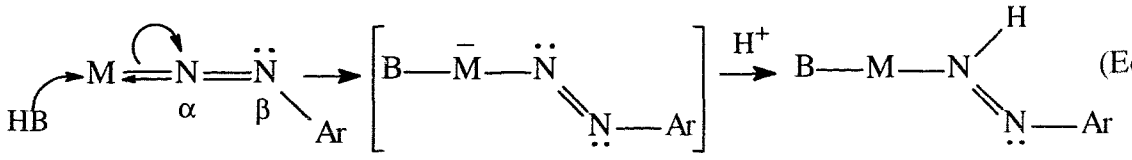
(Eq. 2)



(Eq. 3)

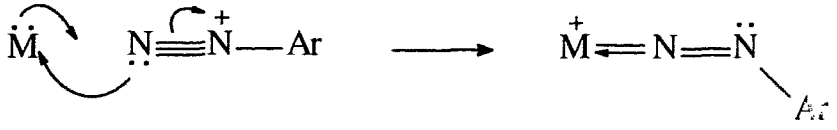
However, certain singly bent aryldiazenido complexes like $[RuCl(CO)_2(PPh_3)_2(N_2Ph)]$[10], $[OsH(CO)(PPh_3)_2(N_2Ph)]$ and $[OsCl(CO)(PPh_3)_2(N_2Ph)]^+$ [6] were found to protonate at N_α, like the doubly bent aryldiazenido case (Eq. 1), but were always accompanied by the coordination of the counteranion in the metal center. It can then be proposed that these singly bent aryldiazenido compounds initially coordinate the

counteranion, and undergo isomerization to yield the doubly bent aryldiazenido ligand in order to maintain the 18 electron system, which is finally protonated at N_α (Eq. 4). Unfortunately, the proposed intermediate in (Eq. 4), *i.e.* the doubly bent aryldiazenido compound, was not isolated. Therefore, isolating this doubly bent aryldiazenido intermediate would not only confirm the proposed scheme (Eq. 4), but more importantly, would provide us with evidence for possible interconversion between the two geometries and perhaps a new synthetic route to doubly bent aryldiazenido compounds.



(Eq. 4)

While there are many examples of complexes with singly bent aryldiazenido geometry, there are very few with doubly bent and only one with a side-on coordination mode.[1,11] The appreciable difference in the number of isolated singly and doubly bent aryldiazenido complexes can be attributed to the differences in their synthesis and stability. As mentioned earlier, singly bent and doubly bent aryldiazenido ligands can be viewed as N_2Ar^+ and N_2Ar^- (bent) ligands respectively. In principle, then, the most direct methods of synthesizing such compounds would be by utilizing the corresponding ions as ligands. In fact, many singly bent aryldiazenido compounds are synthesized in this way by directly employing the N_2Ar^+ ion, as shown below (scheme 1).[3,12,13,14]



(scheme 1)

On the other hand, no N_2Ar^- ion exists in order to synthesize doubly bent aryldiazenido complexes in a simple and direct manner. Instead, present methods of

isolating such compounds employ the N_2Ar^+ ligand in reactions in which a formal transfer of two electrons from the metal to the ligand occurs in the following three ways:

(i) by electrophilic attack of N_2Ar^+ at an electron-rich metal center (scheme 2)[3]

(scheme 2)

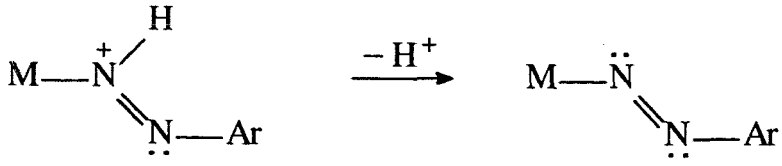
This is by far the most common way of synthesizing the doubly bent aryldiazenido compound (Table 1.1). One well documented example supporting scheme 2 is the coordination of N_2Ph^+ to $[Rh^I(PhP\{(CH_2)_3PPh_2\}_2)(Cl)]$ to yield the square pyramidal complex $[Rh^{III}(PhP\{(CH_2)_3PPh_2\}_2)(Cl)(N_2Ph)][PF_6]$ containing an apical doubly bent aryldiazenido ligand. (Eq. 5).[15,16]

$$[Rh^I(PhP\{(CH_2)_3PPh_2\}_2)(Cl)] \xrightarrow{N_2Ph^+} [Rh^{III}(PhP\{(CH_2)_3PPh_2\}_2)(Cl)(N_2Ph)]^+ \qquad \text{(Eq. 5)}$$

Another is the synthesis of six-coordinate $[Ir^{III}Cl_2(CO)(PPh_3)_2(N_2Ar)]$ by oxidative-addition of N_2Ar^+ and Cl^- to Vaska's complex $[Ir^ICl(CO)(PPh_3)_2]$ (Eq. 6).[5]

$$[Ir^I(Cl)(CO)(PPh_3)_2] \xrightarrow[Cl^-]{N_2Ar^+} [Ir^{III}Cl_2(CO)(PPh_3)_2(N_2Ar)] \qquad \text{(Eq. 6)}$$

(ii) by deprotonation of the respective aryldiazene compounds (scheme 3)[3]

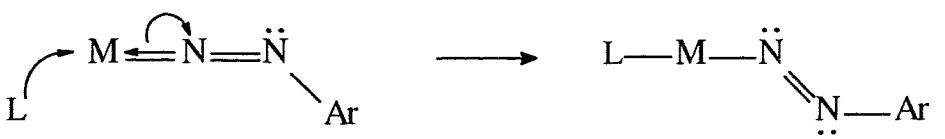


(scheme 3)

The metal hydride complex $[Pt(H)(Cl)(PEt_3)_2]$ undergoes N_2Ph^+ insertion to initially produce the aryldiazene complex $[Pt(Cl)(PEt_3)_2(NHNPh)][BF_4]$.[4] Then, subsequent deprotonation of this compound with $MeCO_2^-$ yields the square planar doubly bent aryldiazenido compound $[Pt(Cl)(PEt_3)_2(N_2Ph)]$ (Eq. 7).[4] Mechanistic details of the N_2Ph^+ insertion into Pt–H bonds,[17] as well as the X-ray crystal structure of this compound,[4] have already been well documented.

$$[Pt(H)(Cl)(PEt_3)_2] \xrightarrow{N_2Ph^+} [Pt(Cl)(PEt_3)_2(NHNPh)]^+ \xrightarrow{MeCO_2^-} [Pt(Cl)(PEt_3)_2(N_2Ph)] \quad \text{(Eq. 7)}$$

(iii) by redistribution of electron density in the formal N_2Ar^+ complexes through an additional ligand coordination (scheme 4)



(scheme 4)

Unlike schemes 2 and 3, a detailed study on systematic interconversion between the singly and the doubly bent aryldiazenido compounds has yet to be accomplished. While some evidence (see Eq. 4) has already indicated the possible isomerization between the two geometries, no well-documented examples exist to this date. Only one paper, by Haymore, *et. al.*,[6] briefly suggests that coordination of a two electron donor ligand at the metal center of a singly bent aryldiazenido complex causes isomerization of the N_2Ar ligand to yield a doubly bent aryldiazenido compound. More specifically, the singly bent aryldiazenido complexes $[M(CO)_2(PPh_3)_2(N_2Ph)][PF_6]$ (M = Os, Ru) react with several coordinating anions to form neutral six-coordinated doubly bent aryldiazenido complexes $[M(L)(CO)_2(PPh_3)_2(N_2Ph)]$ (Eq. 8).[6]

$$[M(CO)_2(PPh_3)_2(N_2Ph)]^+ \xrightarrow{L^-} [M(\mathbf{L})(CO)_2(PPh_3)_2(N_2Ph)]$$

where **L** = F, Cl, Br, I, NCO, N_3, NO_2, HCO_2, CH_3CO_2 ; M = Os
L = Cl, Br, I, NCO ; M = Ru (Eq. 8)

It should be noted that not only are doubly bent aryldiazenido compounds difficult to synthesize but also that they are unstable toward protonation, side reactions, or decomposition. For example, the doubly bent aryldiazenido product in Eq. 8 readily undergoes protonation with even the slightest trace of acid, forming the stable phenyldiazene complex, $[Os(\mathbf{L})(CO)_2(PPh_3)_2(NHNPh)]^+$ [6] (refer to Eq. 1). In another case, $[RhX_2(PPh_3)_2(N_2Ar)]$ (X = Cl or Br) decomposes in an organic solvent by eliminating dinitrogen or by abstracting hydrogen chloride from the solvent.[18] Likewise, $[Ir(Cl)(CO)(PPh_3)_2(N_2Ar)]^+$ decomposes by extruding dinitrogen, or forms an orthometallated aryldiazene species depending on the solvent used.[5,19] As a result, very few doubly bent aryldiazenido compounds have been characterized by IR or NMR spectroscopy and only three such compounds have been characterized by X-ray crystallography (Tables 1.1, 1.2). Tables 1.1 and 1.2 list all the reported doubly bent aryldiazenido compounds to date, and in them the compounds are categorized according to the synthetic route.

As has already been mentioned, isolating doubly bent aryldiazenido compounds via scheme 4 (*i.e.* systematically converting a singly bent system to a doubly bent one) still requires further investigation and there is currently no example in which the X-ray crystal structures of the singly bent aryldiazenido precursor and the doubly bent aryldiazenido complex produced have been done so as to completely document this stereochemical transformation. Previously in our laboratory, a singly bent aryldiazenido system which could potentially and perhaps successfully demonstrate this isomerization had been isolated. The following section provides the details.

Table 1.1 Characterization of Doubly Bent Aryldiazenido Complexes

Complex	Synthetic Route	ν(NN) (cm^{-1})[a]	$\delta^{15}N_{\alpha}$ (ppm)[d,e]	X-ray[f]	Ref.[g]
$[RhCl(PPP)(N_2Ph)][PF_6]$[h]	Electrophilic attack (i)	1561, 1627[b]	137.9	*	16
$[RhCl(diphos)(N_2Ph)][PF_6]$[h]		1493, 1466[b]	224.6		15
$[IrBr(diphos)(N_2Ph)][PF_6]$[i]		1470[b,c]	220.5		15
$RhCl_2(PEtPh_2)_2(N_2Ph)$			241.0		20
$RhCl_2(PPh_3)_2(N_2Ph)$		1545, 1610[b]	298.4		21,22
$RhCl_2(PPh_3)_2(p\text{-}N_2C_6H_4Y)$		*ca.* 1545 - 1620[b]	327.1[k]		21,22
Y = Cl, F, Me, OMe, NO_2					
$IrCl_2(CO)(PPh_3)_2(o\text{-}N_2C_6H_4NO_2)$[j]		1462[b,c]		*	5
$IrCl(X)(L)(PPh_3)_2(p\text{-}N_2C_6H_4Y)$		*ca.* 1461 - 1501[b]	241.4[l]		23
X = Cl, Br, I, N_3, NO_2, NCO					
L = CO, EtNC ; Y = F, H, CH_3					

[a] Solid state measurement of unlabelled compound. [b] Measured in Nujol mulls.
[c] There probably are other bands associated with ν(NN) which are hidden by other interfering bands.
[d] Chemical shifts relative to external neat nitromethane. [e] Refer to ref. 20.
[f] Data available only for the compounds marked (*). For detailed data, refer to Table 3. [g] Reference to preparative and structural information.
[h] Measured at −10°C. [i] $[IrCl(diphos)(N_2Ph)][PF_6]$ also isolated. [j] $IrCl_2(CO)(PPh_3)_2(o\text{-}N_2C_6H_4F)$ also isolated. [k] Data corresponds to Y = NO_2.
[l] Data corresponds to X = Cl ; L = CO ; Y = H.

Table 1.2 Characterization of Doubly Bent Aryldiazenido Complexes

Complex	Synthetic Route	ν(NN) (cm^{-1})	$\delta^{15}N_{\alpha}$ (ppm)[d,e]	X-ray[f,k]	Ref.[g]
$PtCl(PEt_3)_2(p\text{-}N_2C_6H_4Y)$[h]	Deprotonation (ii)	*ca.* 1440 - 1614[b]	285.0[j]	*	24,25
Y = F, H, NO_2					
$OsH(CO)_2(PPh_3)_2(N_2Ph)$		1453[b,c]			6
$RuH(CO)_2(PPh_3)_2(N_2Ph)$		1455[c,i]			6
$OsX(CO)_2(PPh_3)_2(N_2Ph)$	Redistribution (iii)	*ca.* 1440 - 1457[b]			6
X = F, Cl, Br, I , NCO, N_3, NO_2, HCO_2, CH_3CO_2					
$RuX(CO)_2(PPh_3)_2(N_2Ph)$		*ca.* 1414 - 1458[b]			6
X = Cl, Br, NCO, I					
$Cp^*IrH(PPh_3)(p\text{-}N_2C_6H_4OMe)$			271.9		26

[a-g] See Table 1.1 for footnotes. [h] Measured in THF solvent. [i] Measured in perfluorokerosene mulls. [j] Data corresponds to Y = H.
[k] X-ray crystal structure available only for Y = F.

1.2 RESEARCH PROJECT

1.2.1 Background

My research interest arose from the following findings. Previously, Dr. X. Yan in our laboratory isolated a rare hydrido doubly bent aryldiazenido compound [Cp*Ir(PPh$_3$)(H)(*p*-N$_2$C$_6$H$_4$OMe)] **D**, by treating the singly bent aryldiazenido complex [Cp*Ir(PPh$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] **C** with an excess amount of BH$_4^-$ (Eq. 9).[26]

$$\underset{\mathbf{C}}{[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]} \xrightarrow[-10\,^\circ C]{NaBH_4} \underset{\mathbf{D}}{[Cp^*Ir(PPh_3)(H)(p\text{-}N_2C_6H_4OMe)]} \qquad \text{(Eq. 9)}$$

He attempted to synthesize the chloro analogue, [Cp*Ir(PPh$_3$)(Cl)(*p*-N$_2$C$_6$H$_4$OMe)], of the hydrido compound by deprotonation of the aryldiazene complex [Cp*Ir(PPh$_3$)(Cl)(*p*-NHNC$_6$H$_4$OMe)][BF$_4$]. This, however, did not yield the desired product and instead gave [Cp*Ir(PPh$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][Cl][26], *i.e.* simply the chloride salt of the original singly bent aryldiazenido complex (Eq. 10).

$$\underset{\mathbf{C}}{[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]} \xrightarrow[-10\,^\circ C]{HCl(g)} \underset{\text{(Major product)}\ \mathbf{E}}{[Cp^*Ir(PPh_3)(Cl)(p\text{-}NHNC_6H_4OMe)][BF_4]}$$

$$\text{Complex } \mathbf{E} \xrightarrow{NEt_3} \underset{\text{(Major product)}}{[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][Cl]} \qquad \text{(Eq. 10)}$$

Two conclusions were drawn from these results and provided the basis for my research.

i. The singly bent aryldiazenido complex [Cp*Ir(PPh$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] **C**, the starting compound in both Eq. 5 and 6, provides us with a stable 18 electron system, but one with an open face where the second ancillary ligand can attack. We hypothesized that the Lewis base coordination by this singly bent system is forcing the electron density from

the metal center to the N_2Ar^+ group, converting it to a formally one electron, doubly bent aryldiazenido ligand as suggested in scheme 4 and Fig. 1. Therefore, utilizing this stable singly bent system as well as other monophosphine derivatives $[Cp^*Ir(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ may be a route to a series of doubly bent aryldiazenido compounds, which can provide further insight on the systematic conversion of the singly bent to the doubly bent systems.

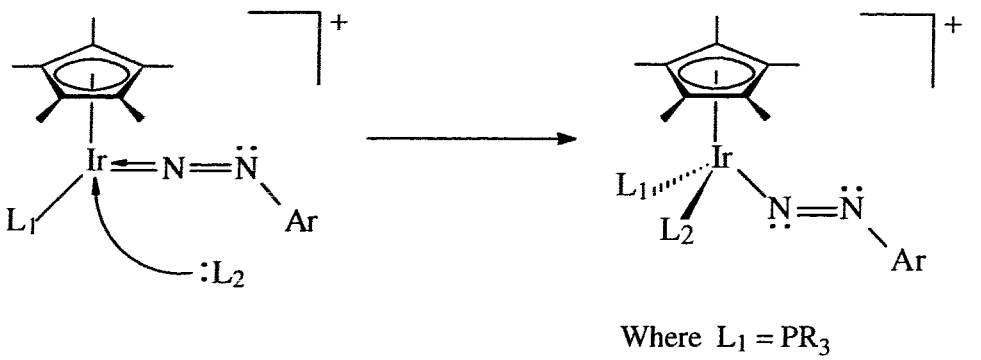


Fig. 1 Proposed synthesis of doubly bent aryldiazenido complexes

ii. The doubly bent system $[Cp^*Ir(PPh_3)(L)(p\text{-}N_2C_6H_4OMe)]^{+,0}$ seems to be isolable only for particular kinds of ligands since the reaction involving L = H (Eq. 9) was successful while using L = Cl (Eq. 10) was not. Thus, it would be noteworthy to investigate what ligands can stabilize the doubly bent aryldiazenido ligand in the system mentioned above, and in analogous derivatives.

1.2.2 Research Outline

Attempts were made to first synthesize new singly bent aryldiazenido compounds of type $[Cp^*Ir(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ by varying the phosphorus ligands. It is recognized that changing the substituents (*i.e.* R groups) on phosphorus ligands correspondingly changes their electronic and steric properties. These electronic and steric effects are quantitatively measured based on the A_1 carbonyl stretching frequencies (ν) in

$Ni(CO)_3L$ complexes (where L = phosphorus ligands) and on the cone angles (θ) of space filling molecular models of the phosphorus ligands (Table 2).[27]

Table 2 Electronic and Steric Parameters of Selected Phosphorus Ligands

PR_3	$\nu(CO)^a$,cm^{-1}	θ, deg
PMe_3	2064.1	118
$P(p\text{-Tol})_3$	2066.7	145
PPh_3	2068.9	145

[a] For $Ni(CO)_3L$ complexes where L = PR_3.

Two phosphorus ligands, $P(p\text{-tol})_3$ and PMe_3, were utilized in the syntheses of new singly bent aryldiazenido compounds since both ligands provide similar, if not better, basicity and cone angle than PPh_3 ligand (Table 2).[27] The result showed that the $P(p\text{-tol})_3$ ligand yielded an expected singly bent aryldiazenido compound $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$, but that PMe_3 directly produced our ultimately desired doubly bent aryldiazenido compound, $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$. Based on these promising results, my research continued into the isolation of several other doubly bent aryldiazenido compounds by systematically converting appropriate singly bent aryldiazenido complexes according to the scheme mentioned in Fig.1.

Since the nature of the ancillary ligand could directly influence the stability and the geometrical preference of the aryldiazenido ligand in the complex, the choice of the second incoming ancillary ligand becomes a crucial factor in systematic conversion of a singly bent aryldiazenido compound to a doubly bent one. A series of phosphorus ligands were initially chosen as the second incoming ligand for various reasons. First, isolation of $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ suggests that two more electrons introduced by the phosphorus ligand provide the 18 electron singly bent compounds with a sufficient electron density around the metal center to push a pair of electrons to the aryldiazenido ligand. Second, the phosphorus ligands, as mentioned earlier, can provide a variety of steric and

electronic effects in a given system[27] and are therefore excellent probes to measure the extent of ligand effects in the system of interest. The choice of second incoming ligands was then further extended to other non-phosphorus ligands such as CO and CN^-, to investigate the types of ligands that can stabilize doubly bent aryldiazenido compounds.

1.3 IMPORTANT TECHNIQUES

Many spectroscopic and structural techniques, in principle, could be used for characterization of transition metal complexes containing the aryldiazenido ligand. However, the most useful methods are X-ray crystallography, infrared spectroscopy and ^{15}N NMR spectroscopy.

1.3.1 X-ray Crystallography

The most reliable method for precisely determining the molecular structure and the coordination mode of the aryldiazenido ligand in a complex in the solid state is single crystal X-ray crystallography. While obtaining a suitable single crystal of the compound is necessary, it is often times difficult to obtain such a crystal, especially for unstable or short-lived compounds, as is the case with most of the known doubly bent aryldiazenido complexes. In fact, most of these are only stable in the solid state and when stored at low temperature in the dark.[5,28] In solution, decomposition of these compounds seems to be promoted by light exposure, ambient temperature or even solvents.[5,18] As one can see from Table 3, typical parameters for the singly bent aryldiazenido compounds are $\angle$ M-N-N = $170^\circ - 180^\circ$, $\angle$N-N-C = $118^\circ - 137^\circ$, and N-N = 1.20 Å (which is close to the typical NN double bond length of 1.23 Å). The M-N bond length is generally in the typical double bond range for the metal in question. For the doubly bent aryldiazenido ligand, these parameters are $\angle$M-N-N = $115^\circ - 125^\circ$, $\angle$ N-N-C = $115^\circ - 120^\circ$, and N-N = 1.17 - 1.19 Å. The M-N distance is in the single bond length range.

Table 3 Structural data for Selected Aryldiazenido Complexes

Complex	M-N (Å)	N-N (Å)	M-N-N (°)	N-N-C(°)	Ref.
$ReCl_2(PMe_2Ph)_3(N_2Ph)^a$	1.77(2)	1.23(2)	173(2)	119(2)	29,30
$[Fe(CO)(PPh_3)_2(N_2Ph)][BF_4]^a$	1.702(6)	1.201(7)	179.2(5)	124.2(6)	31
$RuCl_3(PPh_3)_2(p\text{-}N_2C_6H_4Me)^a$	1.784(5)	1.158(6)	171.9(5)	137.1(5)	32
$[RhCl(PPP)(N_2Ph)][PF_6]^b$	1.961(7)	1.172(9)	125.1(6)	118.9(8)	15
$PtCl(PEt_3)_2(p\text{-}N_2C_6H_4F)^b$	1.97(3)	1.17(3)	118(2)	118(2)	4
$IrCl_2(CO)(PPh_3)_2(o\text{-}N_2C_6H_4NO_2)^b$	2.05(4)	1.19(4)	115(3)	115(3)	5

[a] Singly bent aryldiazenido compounds [b] Doubly bent aryldiazenido compounds

1.3.2 Infrared Spectroscopy

IR spectroscopy is a convenient method which often provides useful structural information on aryldiazenido complexes. While the free aryldiazonium ion (N_2Ar^+) shows a strong infrared absorption frequency near 2260 to 2300 cm^{-1} owing to triple-bond NN stretching, its coordination to a metal centre shifts the NN stretch to a lower frequency, in the range 1400 to 1900 cm^{-1}. Table 4 lists some ν(NN) values for selected aryldiazenido compounds.

There are, however, problems which interfere with effectively diagnosing the coordination modes of aryldiazenido ligands using infrared spectroscopy. First, while the higher values of ν(NN) typically correspond to singly bent aryldiazenido geometry and the lower values correspond to the terminal doubly bent aryldiazenido geometry, there is a considerable region of overlap of ν(NN) for the two different geometries, *i.e.*, the range *ca.* 1500–1680 cm^{-1}. Therefore, these intermediate values of ν(NN) prevent definitive assignment of the coordination modes based on the observed NN frequencies.[15] Moreover, vibrational coupling of the N=N stretch with other vibrational modes of the aryldiazenido ligand also occurs in this region, which further complicates the assignment of the N=N stretch.[6] More specifically, the carbon-carbon skeleton vibration of the aryl ring (1580 – 1600 cm^{-1}) from the N_2Ar ligand falls into the NN vibration range of the singly

bent and the doubly bent aryldiazenido ligands. Consequently, isotopic substitution of N_2Ar using ^{15}N can lead to synchronic shift of C=C and N=N bands (Table 4).

Table 4 NN Stretching Frequencies and ^{15}N Chemical Shift Data for Selected Aryldiazenido Complexes

Complex	ν (NN) (cm^{-1})[c]	δ N_α (ppm)[e,f]	Ref.
$[RuCl_3(PPh_3)_2(N_2Ph)]$[a]	1881	–46.8	18
$[IrCl(PPh_3)_2(N_2Ph)][BF_4]$[a]	1868	–92.1	23
$[RhCl(PMePh_2)_3(N_2Ph)][PF_4]$[a]	1653	109.2	15
$[IrCl_2(CO)(PPh_3)_2(N_2Ph)]$[b]	1470[d]	241.4	23
$[PtCl(PEt_3)_2(N_2Ph)]$[b]	1440[d]	285.0	25
$[RhCl_2(PPh_3)_2(N_2Ph)]$[b]	1545, 1610	298.4	18

[a] Singly bent aryldiazenido compounds
[b] Doubly bent aryldiazenido compounds [c] Solid state measurement of unlabelled compounds
[d] There probably are other bands associated with ν(NN) which are hidden by other interfering bands
[e] Chemical shifts relative to external neat nitromethane, refer to ref.20 [f] Measured in CH_2Cl_2

1.3.3 ^{15}N NMR Spectroscopy

^{15}N NMR spectroscopy is one of the most useful and reliable spectroscopic techniques for studying the coordination mode of aryldiazenido ligands. It not only is relatively simple to synthesize ^{15}N labelled aryldiazenido compounds, but also nitrogen chemical shifts are quite sensitive to the geometric and electronic environment of the aryldiazenido ligand. For example, there is a dramatic difference in $^{15}N_\alpha$ resonances between the aryldiazenido ligands with a singly bent geometry and a doubly bent geometry (Table 4).[20,33] For doubly bent aryldiazenido ligands, the $^{15}N_\alpha$ resonances occur at high δ values from 290 to 200 ppm, while for singly bent aryldiazenido ligands δ ($^{15}N_\alpha$) occurs in the region from 100 to –47 ppm (all with respect to $MeNO_2$ as a standard).[1] The $^{15}N_\alpha$ resonance of the free aryldiazonium ion $^{15}N{\equiv}NAr^+$ also falls in this region (δ –66.9). Upon protonation at N_α in doubly bent aryldiazenido complexes, a dramatic upfield shift of this

nitrogen by ~300 ppm is observed. It should be noted that due to the low natural abundance (0.37 %) and the low, negative, gyromagnetic ratio of ^{15}N (spin 1/2), it is difficult to observe ^{15}N NMR without enriching the complex with ^{15}N at the desired nitrogens. For our purposes, the aryldiazenido ligand is usually enriched only at the α nitrogen. This is accomplished by synthesizing $[p\text{-}^{15}N{\equiv}NC_6H_4OMe]^+$ from *p*-anisidine and the commercially available $Na^{15}NO_2$ (95% ^{15}N enriched).

CHAPTER II RESULTS

2.1 PREPARATION OF THE STARTING MATERIALS

The starting materials $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B** [26,34] and $[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C** [26] were prepared according to the methods developed by Dr. X. Yan in our laboratory. The synthetic routes are summarized in Fig. 2. After synthesizing $[Cp^*IrCl_2]_2$ [35] and then $[Cp^*Ir(C_2H_4)_2]$ [36] by the respective literature method, *p*-methoxybenzenediazonium tetrafluoroborate was introduced to yield compound **B**. For the synthesis of **C**, either of the following two methods can be employed.[37]

Method 1. Introduce PPh_3 to $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B**.

Method 2. Introduce PPh_3 and $[p\text{-}N_2C_6H_4OMe][BF_4]$ to $[Cp^*Ir(C_2H_4)_2]$ **A**.

The second method is preferred for the synthesis of $[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C** for its convenience and yield,[37] and is the method used in this work. For the syntheses of ^{15}N labelled starting compounds, $[p\text{-}^{15}NNC_6H_4OMe][BF_4]$ was utilized.

2.2 SYNTHESIS AND CHARACTERIZATION OF SINGLY BENT ARYLDIAZENIDO COMPOUND $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1)

A new singly bent aryldiazenido compound $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1) was isolated as an orange powder when $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B** was treated with equimolar $P(p\text{-tol})_3$ in acetone at 0°C (Fig. 3). Recrystallization from acetone-hexane gave orange crystals suitable for X-ray crystal analysis.

Upon substituting the C_2H_4 ligand with $P(p\text{-tol})_3$, a new $\nu(NN)$ band in the IR spectrum appeared at 1709 cm^{-1} (EtOH). This falls within the typical range for the terminally coordinated singly bent aryldiazenido ligand. A $^{15}N_\alpha$-enriched sample showed an isotopic shift of 35 cm^{-1} (Fig. 4).

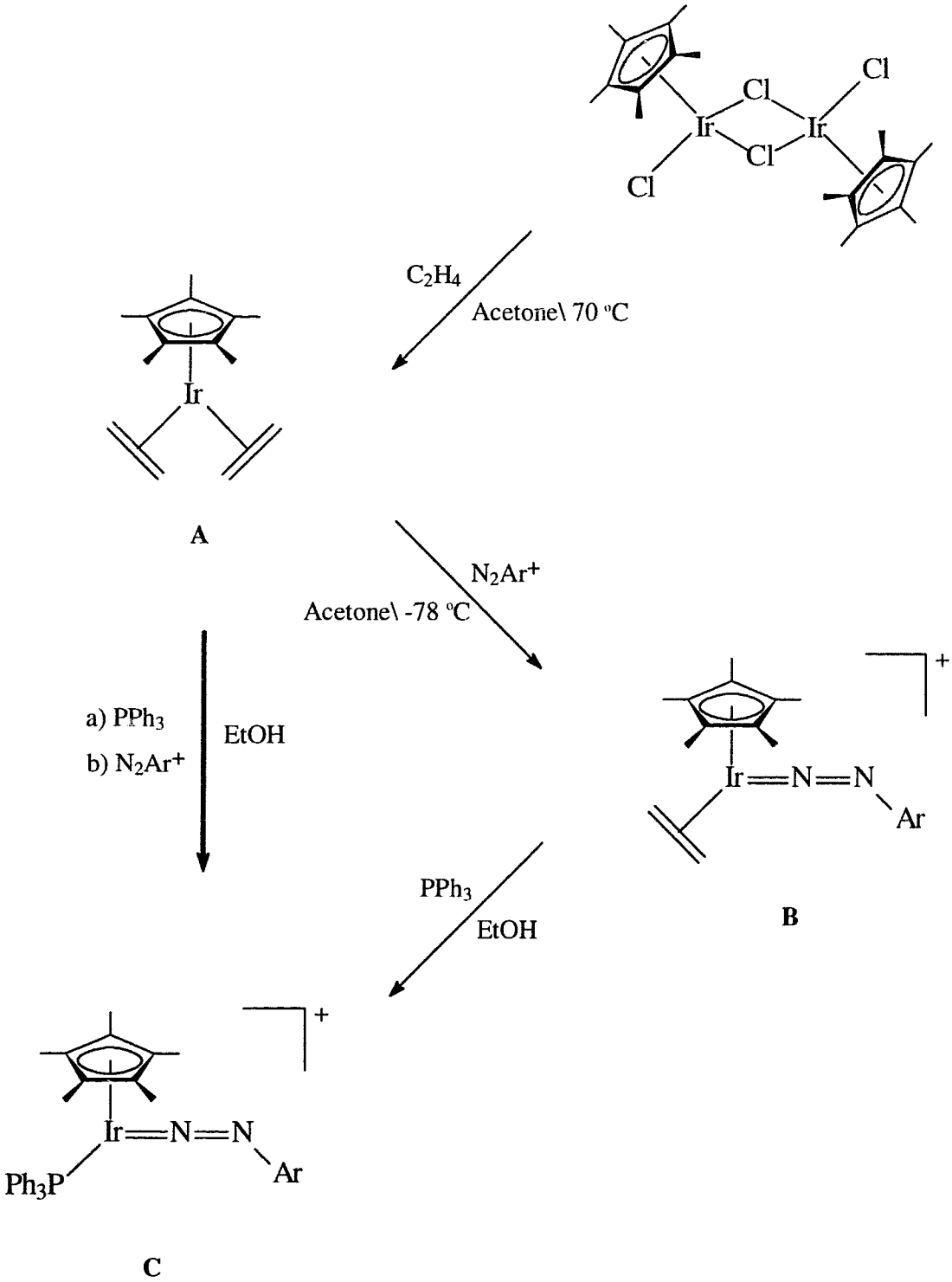


Fig. 2 Synthetic scheme for starting complexes (Ar = *p*-C_6H_4OMe)

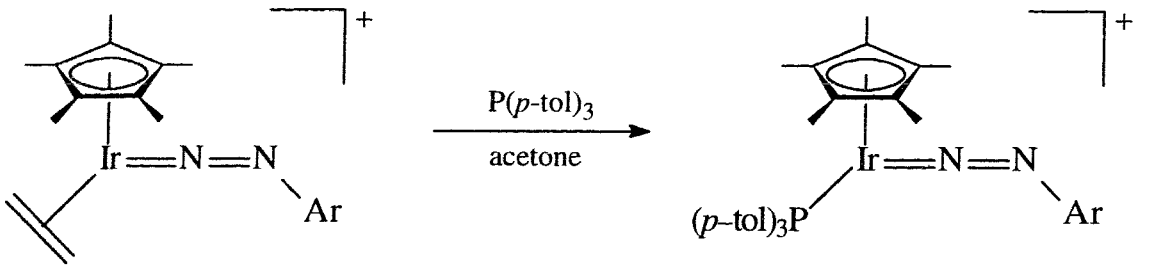


Fig. 3 Synthesis of $[Cp^*Ir\{P(p\text{-tol})_3\}(N_2Ar)][BF_4]$ (1) (Ar = p-C_6H_4OMe)

In the ^1H NMR spectrum of (1), $P(p\text{-tol})_3$ coordination is indicated as a broad singlet at δ 2.35 (integral 9H), corresponding to the $P(p\text{-tol})_3$ methyl groups (Fig. 5). The broad peak seems to suggest that the $P(p\text{-tol})_3$ ligand in solution is nonrigid and undergoes a dynamic process. While the phenyl derivatives of the phosphorus ligands have often exhibited hindered rotation about the metal-phosphorus bond,[38,39,40] the variable temperature ^1H NMR studies investigating the similar effect in (1) showed no evidence of restricted rotation about the M-P bond, *i.e.* the resonance at δ 2.35 showed no further broadening upon cooling to –90 °C. The coupling pattern of Cp* in the ^1H NMR spectrum also gives a good indication of the number of phosphorus ligands coordinated to the system of interest. Indeed, the resonance corresponding to the Cp* methyl group appeared as a doublet at δ 2.04 (integral 15H) resulting from coupling to the phosphorus nucleus (Fig. 5). The p-methoxyphenyldiazenido group in the compound gave apparent doublets at δ 6.94 and δ 7.10 for the aryl group and a singlet at δ 3.87 for the OMe protons. The singly bent coordination mode of the aryldiazenido ligand in (1) was unambiguously illustrated by the $^{15}N_\alpha$ resonance (from the ^{15}N NMR spectrum) at δ 33.68, which is well within the region assigned to singly bent aryldiazenido compounds. The ^{31}P-$^{15}N_\alpha$ coupling constant from the ^{15}N NMR resonance [$J_{P\text{-}^{15}N}$ = 6 Hz] well corresponds with that from the $^{31}P\{^1H\}$ NMR (Fig. 6). These results were similar to those obtained from the $^{31}P\{^1H\}$ and ^{15}N NMR spectra of $[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C** [$J_{P\text{-}^{15}N}$ = 7 Hz].

The FABMS of (1) displays the parent peak for the cation at m/z 767, along with the fragments formed by the loss of $N_2C_6H_4OMe$ and 1H (from Cp*) at m/z 631 and the loss of P(*p*-tol)$_3$ and 2H (from Cp*) at m/z 461.

It should be noted that introducing an exact stoichiometric amount of P(*p*-tol)$_3$ to the system is a crucial factor in successfully synthesizing (1). Addition of more than one equivalent of P(*p*-tol)$_3$ resulted in a brown product, which according to ^{1}H NMR analysis, contained many impurities.

When compound (1) was synthesized by introducing P(*p*-tol)$_3$ and aryldiazonium salt to [Cp*Ir(C_2H_4)$_2$] **B** (the method favoured for the synthesis of [Cp*Ir(PPh_3)(*p*-$N_2C_6H_4OMe$)]$^+$), a by-product identified as [(*p*-tol)$_3$P–(*p*-$N_2C_6H_4OMe$)]$^+$ was invariably observed in the ^{1}H NMR spectrum (Eq. 7). The identity of the [(*p*-tol)$_3$P–(*p*-$N_2C_6H_4OMe$)]$^+$ adduct was determined by comparing this ^{1}H NMR spectrum with the spectrum for the product obtained by reacting P(*p*-tol)$_3$ and [*p*-$N_2C_6H_4OMe$]$^+$.

$$[Cp^*Ir(C_2H_4)_2] + P(p\text{-tol})_3 + [p\text{-}N_2C_6H_4OMe]^+ \longrightarrow [Cp^*Ir\{P(p\text{-tol})_3\}N_2Ar]^+ + [(p\text{-tol})_3P\text{–}(p\text{-}N_2C_6H_4OMe)]^+ \qquad \text{(Eq. 7)}$$

The X-ray crystal structure of compound (1) was kindly determined by Dr. R. J. Batchelor in Professor F. W. B. Einstein's laboratory. It clearly illustrates a singly bent geometry of the aryldiazenido group in (1). Detailed discussion will be given in section 2.3.5 of this chapter.

The spectroscopic data characterizing (1) and the other newly synthesized compounds are summarized in Table 5. The data corresponding to the starting materials [Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4OMe$)][BF_4] **B** and [Cp*Ir(PPh_3)(*p*-$N_2C_6H_4OMe$)][BF_4] **C** are also included for comparison.

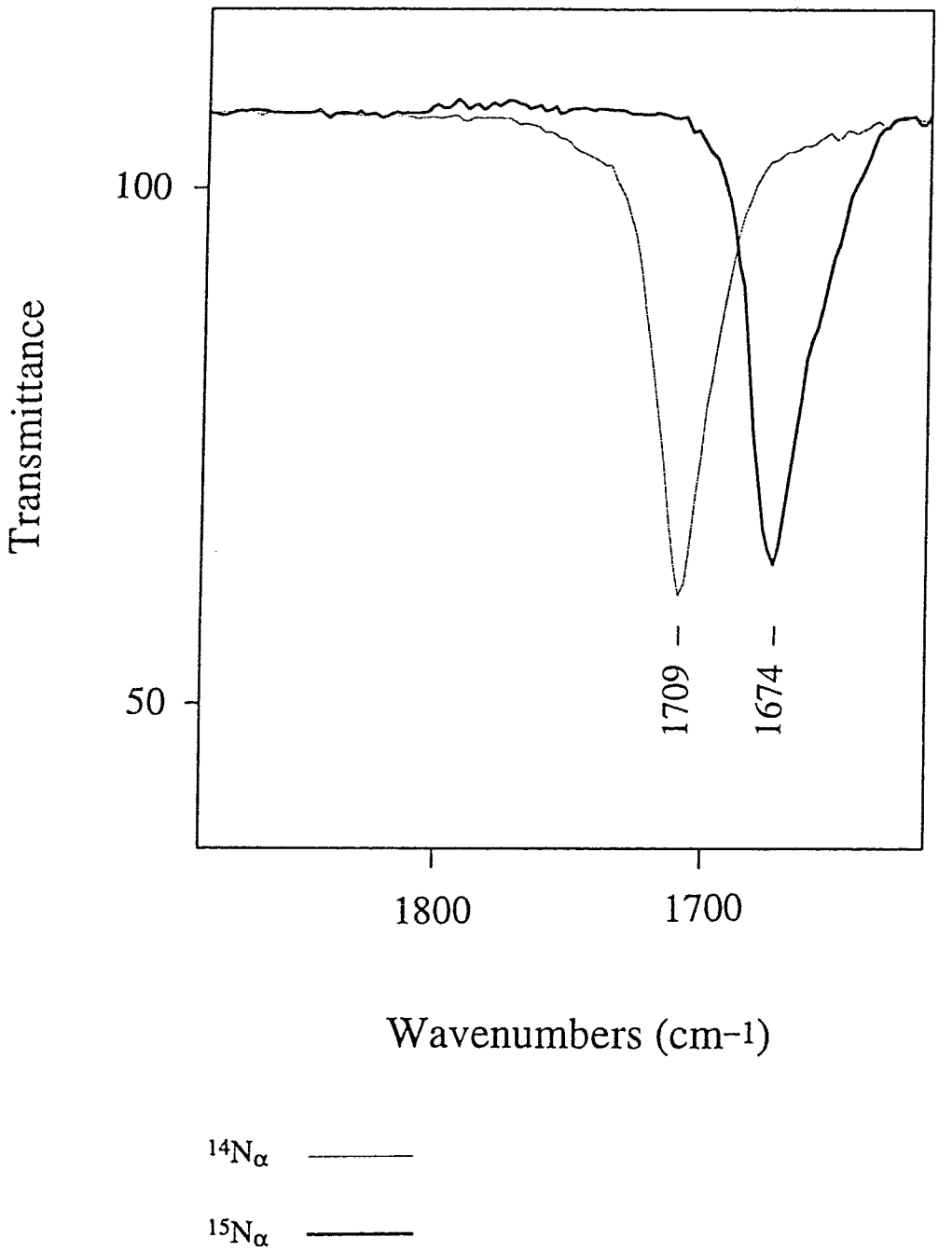
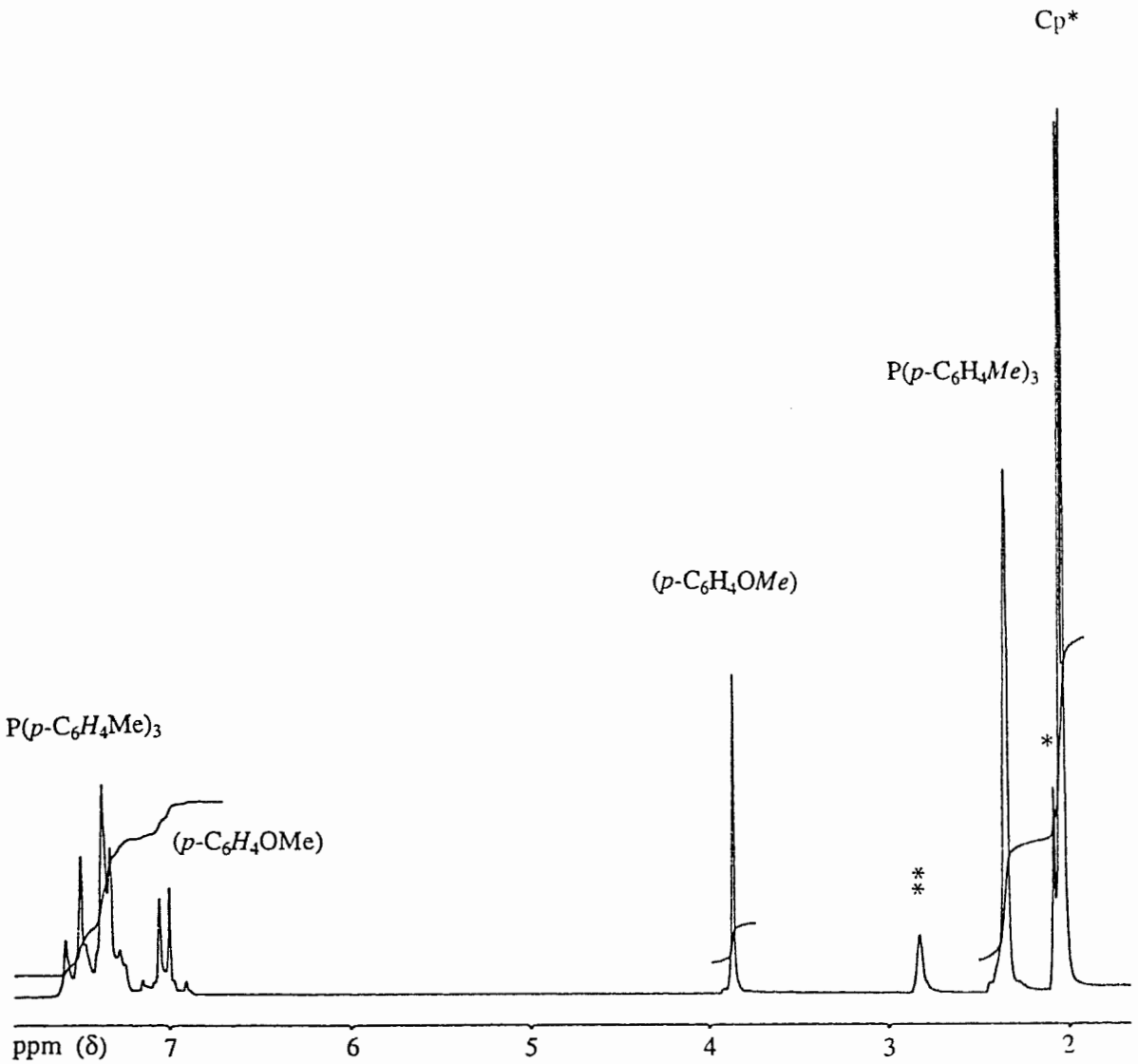


Fig. 4 IR spectrum of $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1) in ethanol



* solvent resonance. ** water resonance.

Fig. 5 100 MHz ^{1}H NMR spectrum of $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1) in acetone-d_6

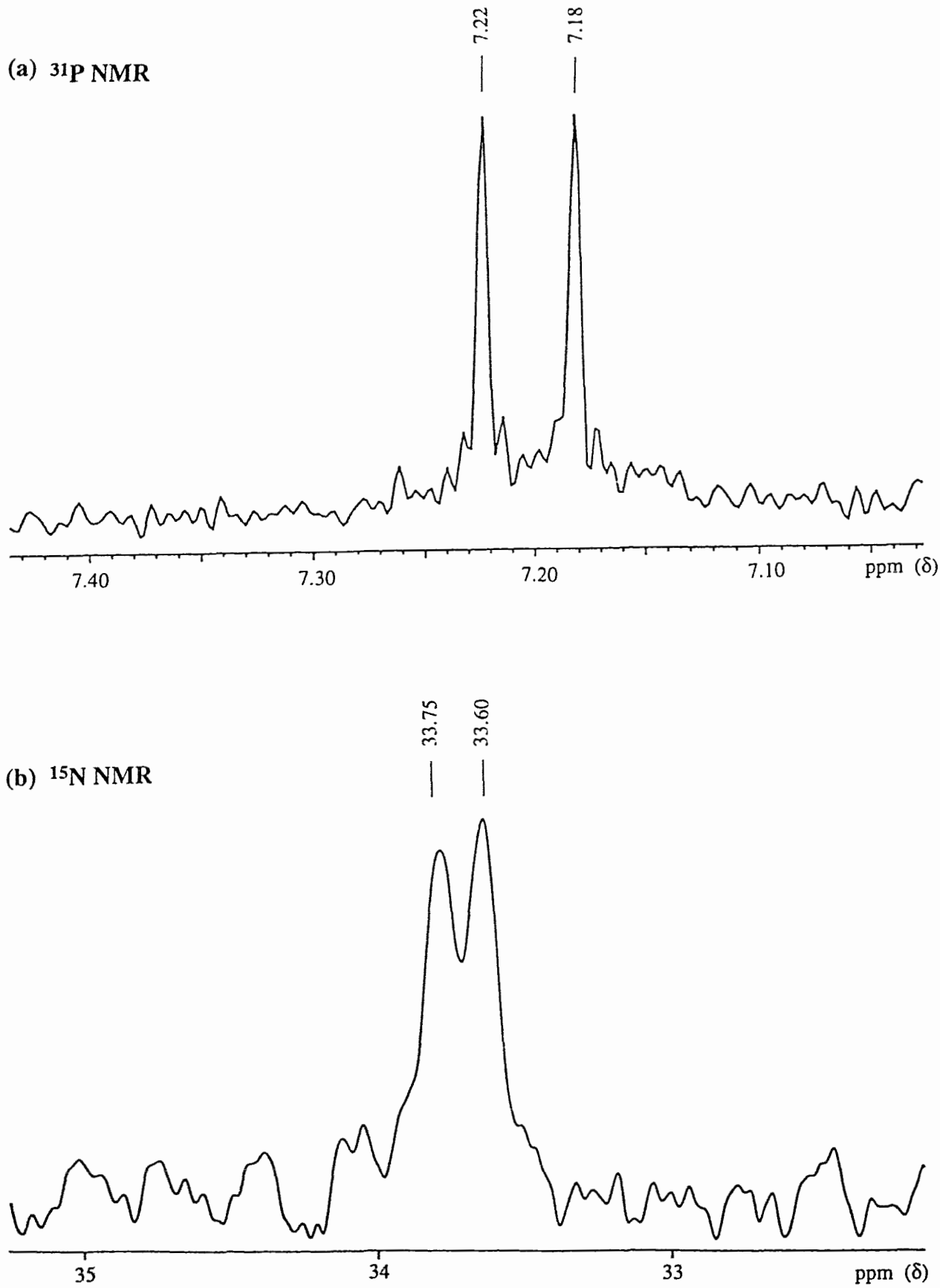


Fig. 6 162 MHz $^{31}P\{^{1}H\}$ and 40.5 MHz ^{15}N NMR spectra of $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1)

Table 5 Summary of ^{1}H (100 MHz), ^{15}N (40.5 MHz) and $^{31}P\{^{1}H\}$ (162 MHz) NMR Data

Complex[a,b]	δ Cp* (ppm)[c]	^{15}N NMR (ppm)[d]	$^{31}P\{^{1}H\}$ NMR (ppm)[e]
(B) $[Cp^*Ir(C_2H_4)N_2Ar]^+$	2.32 s	−2.26 s	——
(C) $[Cp^*Ir(PPh_3)(N_2Ar)]^+$	2.12 d	33.23 d	9.57 d
(1) $[Cp^*Ir\{P(p\text{-tol})_3\}(N_2Ar)]^+$	2.04 d	33.68 d	7.48 d
(2) $[Cp^*Ir(PMe_3)_2(N_2Ar)]^+$	1.86 t	243.1 s	−37.73 s
(3) $[Cp^*Ir(PPh_3)(PMe_3)(N_2Ar)]^+$	1.47 t	234.1 s	−3.31 d [PPh_3]; −36.20 d [PMe_3]
(4) $[Cp^*Ir\{P(p\text{-tol})_3\}(PMe_3)(N_2Ar)]^+$	1.46 t	236.1 s	−5.39 d [$P(p\text{-tol})_3$]; −36.03 d [PMe_3]
(5) $[Cp^*Ir(diphos)(N_2Ar)]^+$	1.55 t	229.0 s	43.84 s
(6) $[Cp^*Ir(PPh_3)(CO)(N_2Ar)]^+$	1.77 d	200.3 s	2.52 s
(7) $[Cp^*Ir(PPh_3)(CN)(N_2Ar)]$	1.48 d	247.5 s	6.99 s

[a] Ar = (p-C_6H_4OMe) [b] (B) to (1) are singly bent aryldiazenido Complexes; (2) to (7) are doubly bent aryldiazenido complexes.
[c] Measured in acetone-d_6 at room temperature. [d] Measured in acetone-d_6 referenced to external $MeNO_2$; ^{15}N enriched at N_α only.
[e] Measured in acetone-d_6 referenced to external 85% H_3PO_4; $^{15}N_\alpha$ labelled sample used.

2.3 SYNTHESES AND CHARACTERIZATION OF DOUBLY BENT ARYLDIAZENIDO COMPOUNDS OF TYPE $[(\eta^5\text{-}C_5Me_5)Ir(L_1)(L_2)(p\text{-}N_2C_6H_4OMe)][BF_4]$

Several new iridium doubly bent aryldiazenido compounds were synthesized by introducing a stoichiometric amount of PR_3 (PR_3 = PMe_3, $Ph_2PC_2H_4PPh_2$), CO, and CN^- to the solution of the singly bent aryldiazenido compound $[Cp^*Ir(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ [PR_3 = PPh_3, $P(p\text{-tol})_3$], or to its precursor $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B** (Fig. 7).

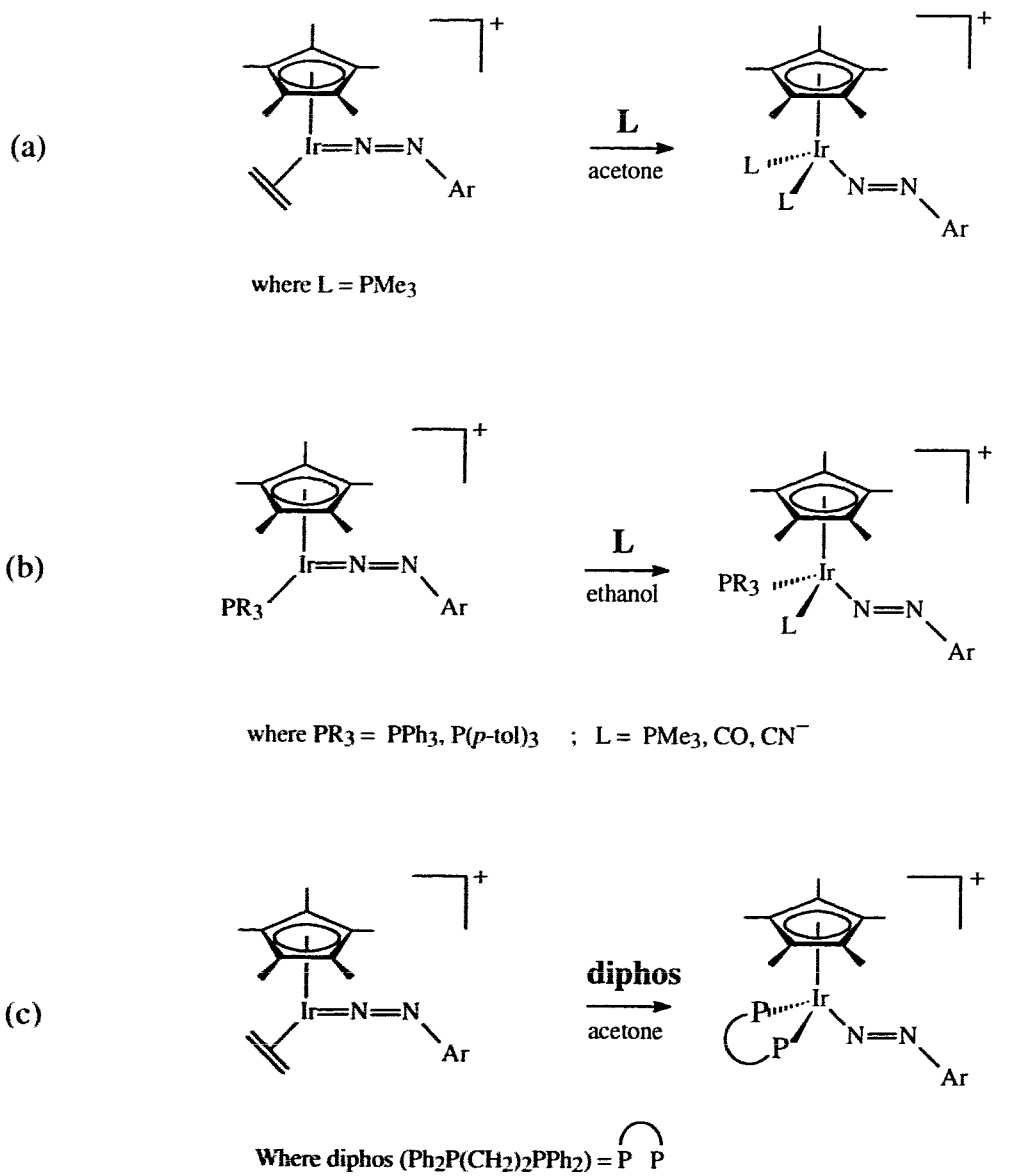


Fig. 7 Syntheses of doubly bent aryldiazenido compounds (Ar = p-C_6H_4OMe)

2.3.1 $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2)

When an excess amount of PMe_3 was added to $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B**, instead of the expected singly bent aryldiazenido compound $[Cp^*Ir(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$, the bis PMe_3 coordinated compound $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2) was isolated, implying that a doubly bent aryldiazenido complex has been formed (Fig. 7a). Recrystallization from acetone-hexane yielded reddish orange crystals suitable for X-ray crystal structure analysis.

It should be noted that synthesis of (2) could not be monitored by IR since the reaction solvent, acetone, shows a strong band corresponding to ν(CO) at ~1700 cm^{-1}, occurring in the same region expected for ν(NN) from the singly bent N_2Ar ligand. Use of ethanol as a reaction solvent produced many impurities according to the ^1H NMR spectrum. Any chlorinated solvent (*i.e.* CH_2Cl_2, $CHCl_3$) also inevitably resulted in the formation of a by product, which according to EIMS and computer simulation, was identified as $[Cp^*Ir(PMe_3)Cl_2]$ (m/z 474).

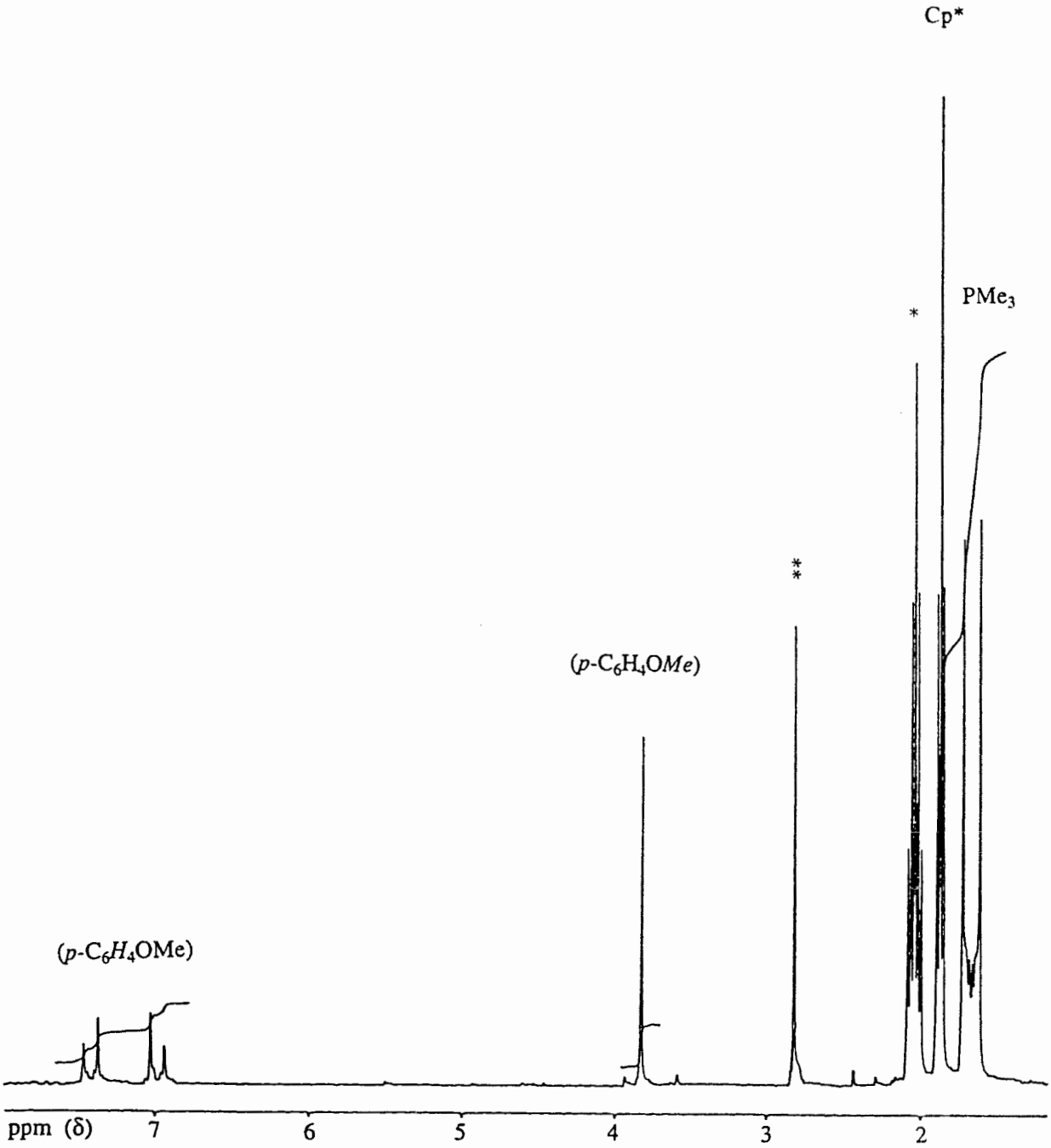
As mentioned earlier, the coupling pattern of Cp* in the ^1H NMR spectrum is diagnostic of the number of phosphorus ligands coordinated to the metal center. So then, a triplet resonance at δ 1.86 corresponding to the Cp* methyl protons for (2) indicates coupling to two chemically identical phosphorus nuclei (Fig. 8). The presence of two phosphorus ligands is further supported by a virtually coupled doublet PMe_3 resonance at δ 1.66 with an integration of 18 H [$J_{P\text{-}H}$ = 10 Hz] (Fig. 8). One sharp resonance at δ −37.73 in the proton decoupled ^{31}P NMR spectrum is consistent with the coordination of two chemically equivalent phosphorus ligands (Fig. 9a). As expected, the ^{15}N NMR spectrum of (2) gave a single $^{15}N_\alpha$ resonance at δ 243.1, which is in the typical chemical shift range for a doubly bent aryldiazenido ligand (Fig. 9b). Note the large chemical shift difference (*i.e.* over 200 ppm) from the singly bent aryldiazenido case (Table 5). Another usual feature exhibited by doubly bent aryldiazenido compounds, and observed here also, is the absence of ^{31}P–^{15}N coupling in the ^{15}N and $^{31}P\{^1H\}$ NMR spectra (Fig. 9).[6,37]

The FAB MS spectrum of (2) gave a parent peak at m/z 615 for the cation, followed by peaks at m/z 539, and m/z 480 which are consistent with the loss of two PMe_3 ligands sequentially. The X-ray crystal structure of (2), included in section 2.3.6, unambigously confirms the doubly bent geometry of the aryldiazenido ligand.

2.3.2 [Cp*Ir(PPh$_3$)(PMe$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (3) and [Cp*Ir{P(*p*-tol)$_3$}(PMe$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$](4)

Several new doubly bent aryldiazenido compounds have been synthesized according to the method proposed in Fig. 1. Treating both [Cp*Ir(PPh$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] **C** and [Cp*Ir{P(*p*-tol)$_3$}(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (1) with a slight excess of PMe_3 resulted in the coordination of one equivalent of PMe_3 and yielded the expected doubly bent aryldiazenido compounds [Cp*Ir(PPh$_3$)(PMe$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (3) and [Cp*Ir{P(*p*-tol)$_3$}(PMe$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (4), respectively (Fig. 7b). The syntheses of both compounds (3) and (4) were monitored by IR spectroscopy. The ν(NN) bands at 1701 and 1709 cm^{-1} each corresponding to the singly bent aryldiazenido compounds **C** and (1) disappeared and no other bands that could be assigned to ν(NN) in the usual singly bent region (1600–2100 cm^{-1}) were observed. Due to the fact that the typical NN stretching frequency region for the doubly bent structure (1400 – 1600 cm^{-1})[1] was obscured by the aromatic bands in our system, no specific ν(NN) band could be assigned for (3) and (4).

The coordination of two phosphorus ligands in (3) and (4) is supported by apparent triplet Cp* methyl resonances shown at δ 1.47 and δ 1.46, respectively, in the ^{1}H NMR spectra [$J_{P\text{-}H}$ = 2 Hz]. Coordination of only one equivalent of PMe_3 in (3) and (4), as opposed to two equivalents of PMe_3 in compound (2) is easily distinguished by differences in the PMe_3 integrations (*i.e.* 9H vs 18H). The presence of two different phosphorus ligands in (3) and (4) is evident from the two sharp doublets in each of the ^{31}P{^{1}H} NMR spectra, illustrating P-P coupling between the two phosphorus atoms (Figs. 10, 11).



* solvent resonance ** water resonance.

Fig. 8 **100 MHz ^{1}H NMR spectrum of $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2) in acetone-d_6**

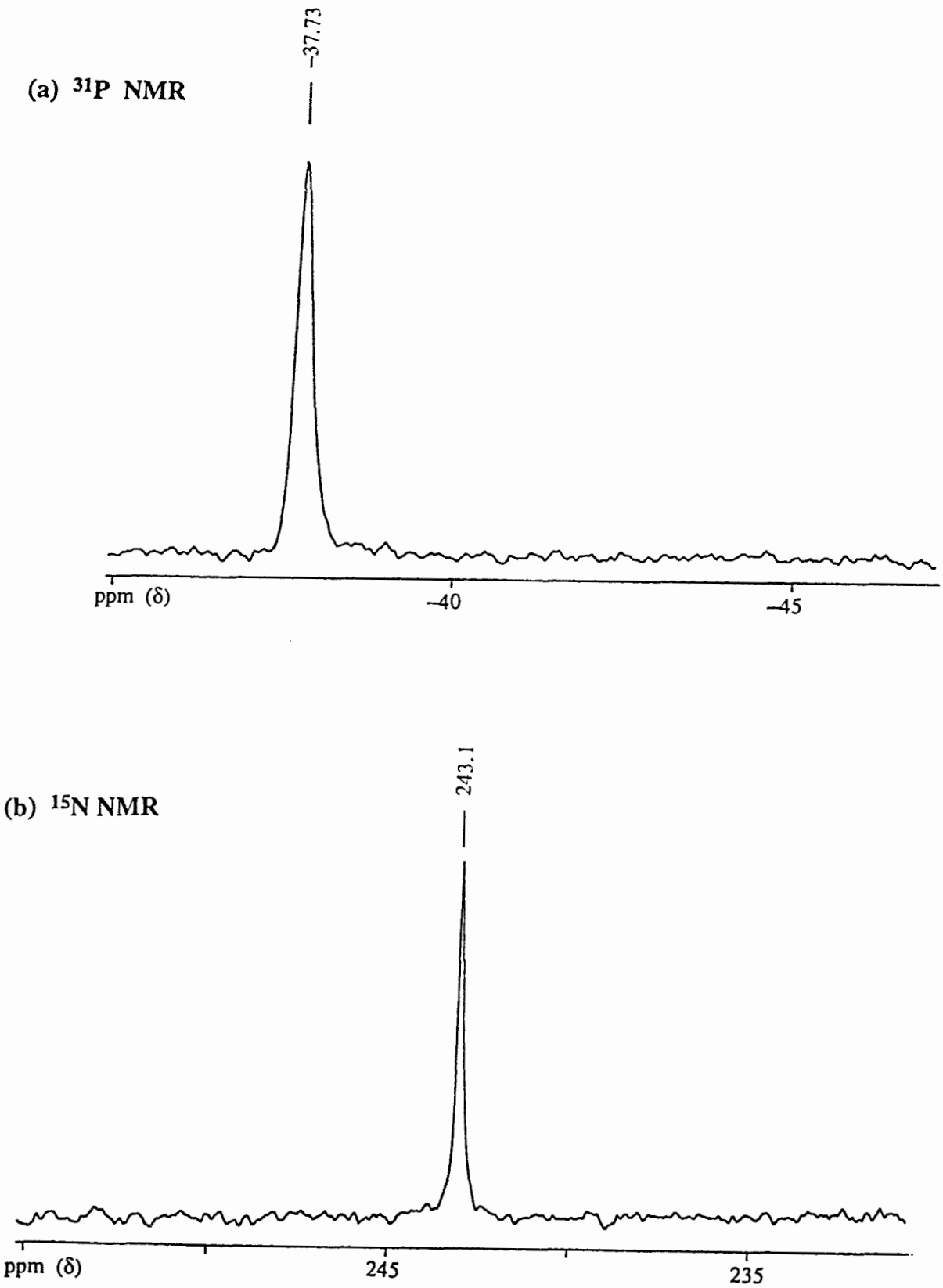


Fig. 9 162 MHz $^{31}P\{^1H\}$ and 40.5 MHz ^{15}N NMR Spectra of $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2)

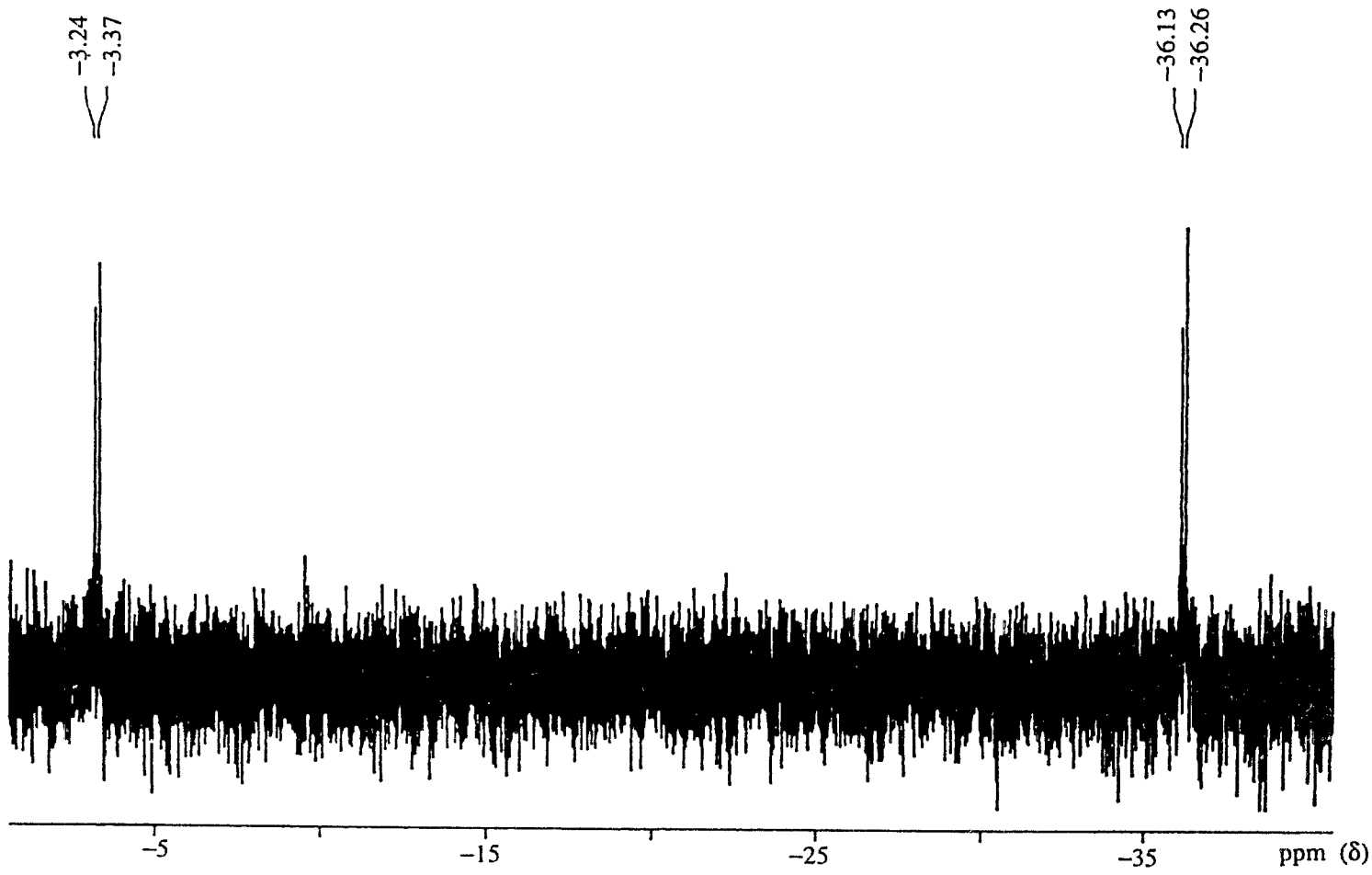


Fig. 10 162 MHz $^{31}P\{^{1}H\}$ NMR spectrum of $[Cp^{*}Ir(PPh_3)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (3)

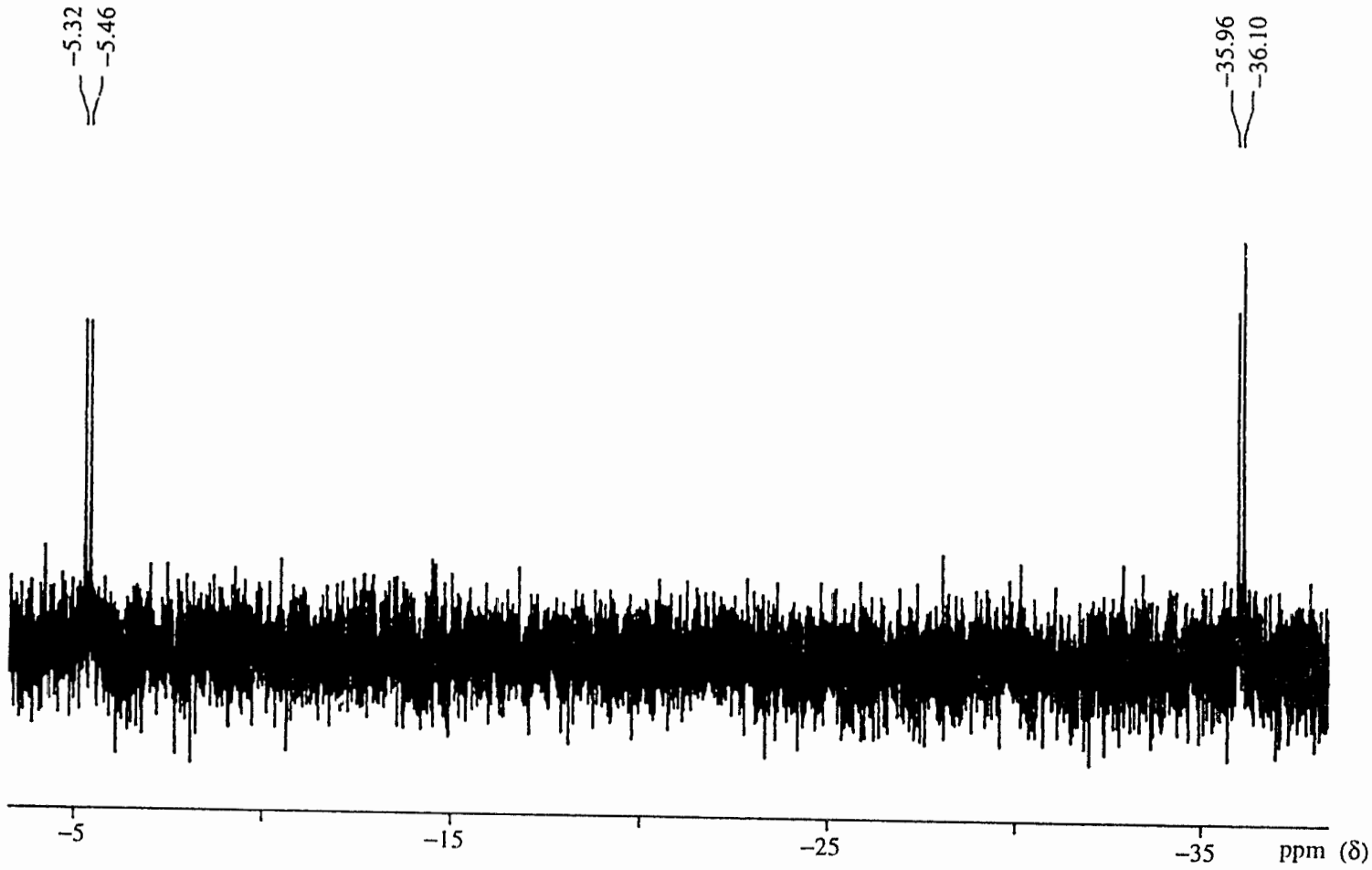


Fig. 11 162 MHz $^{31}P\{^{1}H\}$ NMR spectrum of $[Cp^{*}Ir\{P(p\text{-tol})_3\}(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (4)

The PPh_3 and PMe_3 resonances of (3) each appeared at δ −3.31 and δ −36.20 and the $P(p\text{-tol})_3$ and PMe_3 resonances of (4) appeared at δ −5.39 and δ −36.03. The N_α chemical shifts of (3) and (4) in the ^{15}N NMR spectra occured at δ 234.1 and δ 236.1, clearly indicating the doubly bent nature of aryldiazenido ligands in each case.

2.3.3 [Cp*Ir(diphos)(*p*-$N_2C_6H_4OMe$)][BF_4] (5)

[Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4OMe$)][BF_4] **B** was treated with the bidentate ligand, $Ph_2PC_2H_4PPh_2$ (diphos) to yield the doubly bent aryldiazenido compound (5) (Fig. 7c). A triplet resonance for the Cp* methyl protons at δ 1.55 in the ^1H NMR, and a single resonance at δ 43.84 in the $^{31}P\{^1H\}$ NMR both indicate the coordination of two chemically identical phosphorus atoms. The doubly bent aryldiazenido ligand geometry in (5) is confirmed by the N_α chemical shift of δ 229.0 observed in the ^{15}N NMR spectrum.

2.3.4 [Cp*Ir(PPh_3)(CO)(*p*-$N_2C_6H_4OMe$)][BF_4] (6) and [Cp*Ir(PPh_3)(CN)(*p*-$N_2C_6H_4OMe$)] (7)

To further establish a trend of ligands that can potentially stabilize doubly bent aryldiazenido compounds, a strong electron withdrawing ligand, CO, was reacted with the singly bent aryldiazenido compound [Cp*Ir(PPh_3)(*p*-$N_2C_6H_4OMe$)][BF_4] **C**. Upon introducing CO to **C**, the IR spectrum showed the complete disappearance of the ν(NN) band at 1701 cm^{-1} (in EtOH) due to the singly bent aryldiazenido compound **C** and a concurrent growth of a ν(CO) band at 2039 cm^{-1}, indicating CO coordination (Fig. 7b). The ^1H NMR spectrum of (6) showed a slight change in the chemical shifts from that observed in **C**. The $^{31}P\{^1H\}$ NMR spectrum showed a resonance at δ 2.52 corresponding to coordinated PPh_3. Finally, a single resonance at δ 200.3 in the ^{15}N NMR spectrum confirms the doubly bent N_2Ar ligand geometry in (6).

Another strong π acid ligand, CN^- was also introduced to a solution of [Cp*Ir(PPh_3)(*p*-$N_2C_6H_4OMe$)][BF_4] **C** and yielded a yellowish orange precipitate,

proposed to be [Cp*Ir(PPh_3)(CN)(*p*-$N_2C_6H_4OMe$)] (7) (Fig. 7b). Again, the ^1H NMR spectrum of (7) showed only a slight change in the chemical shifts compared with the ^1H NMR spectrum of **C** before CN^- addition. The $^{31}P\{^1H\}$ (δ 6.99), and $^{15}N_\alpha$ (δ 247.5) NMR spectra indicated the presence of coordinated PPh_3 and a doubly bent N_2Ar ligand, respectively.

Unfortunately, the isolated product had a very low solubility in commonly used solvents such as ethanol, acetone, hexane, or diethyl ether. The inability to find a suitable solvent that would satisfactorily dissolve the isolated product interfered with the characterization of the compound. For example, the concentration of the sample in acetone-d_6 was sufficient for ^1H, $^{31}P\{^1H\}$, and ^{15}N NMR (95% ^{15}N enriched sample used) analysis, but not for a good quality $^{13}C\{^1H\}$ NMR analysis. The spectrum obtained from a $^{13}C\{^1H\}$ NMR overnight run showed no observable resonance assignable to carbon of a coordinated CN in the region *ca.* δ 140 to 180.[41,42] Also, many unassignable resonances other than the expected resonances were observed, suggesting that the product had decomposed to other unknown compounds. Only a limited amount of the sample (7) was dissolved in ethanol, and the IR spectrum of this solution showed a weak band at about 2108 cm^{-1}, assigned to ν(CN) band.

EI MS data did not give a parent peak, but gave a peak at m/z 723 assigned to the loss of CN, accompanied by the loss of 2H from Cp*. Despite some limitations, the data thus far accumulated for (7) suggest its identity as the neutral complex [Cp*Ir(PPh_3)(CN)(*p*-$N_2C_6H_4OMe$)].

2.3.5 X-ray Structure of [Cp*Ir{P(*p*-tol)$_3$}(*p*-$N_2C_6H_4OMe$)][BF_4] (1)

An orange crystal was selected from the sample of (1) and its structure was determined by X-ray crystallography by Dr. R. J. Batchelor in Professor F. W. B. Einstein's Laboratory. The perspective view of (1) and the atomic labelling scheme is shown in Fig.12. The crystal structure of (1) consists of an assemblage of discrete cations,

$[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)]^+$, and anions, $[BF_4]^-$. The geometry of the cation can be described as either a "half sandwich" or a "two-legged piano-stool" structure where N_2Ar and $P(p\text{-tol})_3$ ligands represent the "legs" with the P–Ir–N(1) bond angle of 87.9(2)°. The Cp–Ir–N(1) and Cp–Ir–P bond angles are each 139.4° and 132.5°, where Cp here denotes the centroid of the C_5Me_5 ring. The Cp* ligand is bonded to the iridium in a η^5–coordination mode. The bond lengths from the five carbon atoms in the Cp* ring to iridium range from 2.215(8) to 2.228(7) Å, with the exception of Ir-C(3) which is 2.263(7) Å. The slight deviation in the Ir-C(3) bond length can be attributed to the steric influence of the bulky $P(p\text{-tol})_3$ ligand where the phenyl rings exhibit the usual propeller structure. The $P(p\text{-tol})_3$ ligand is pseudo-trans to the aryldiazenido ligand and is bound to Ir with an Ir-P bond length of 2.322(2) Å. The aryldiazenido ligand in this compound clearly has a singly bent geometry, in agreement with the reported values of ν(NN) and the $^{15}N_\alpha$ chemical shift. The Ir-N(1)-N(2) and N(1)-N(2)-C(21) bond angles are respectively 177.7(6)° and 120.2(7)°. The Ir-N(1) and N(1)-N(2) distances are expected values of 1.811(6) Å and 1.205(8) Å. This suggests approximate sp hybridization about N(1) and sp^2 hybridization about N(2). As observed for the singly bent aryldiazenido complex $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B**, the N_2Ar plane is pseudo-parallel with the Cp* plane. The coplanarity of N_2Ar group [with N(1)-N(2)-C(21)-C(22) and N(1)-N(2)-C(21)-C(26) torsion angles of –8.6(4)° and 167.7(10)°, respectively] suggests optimal overlap of N(2) and phenyl ring π orbitals.

2.3.6 X-ray Structure of $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2)

A single crystal X-ray structure analysis on $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2) was also carried out by Dr. R. J. Batchelor. It revealed that the cation has the general stereochemistry shown in Fig. 13. The geometry of the cation of (2) can again be described as "half sandwich" or "piano-stool" structure but with three "legs". The two phosphine groups are located below the Cp* ring but cis to the aryldiazenido ligand. The Ir-P(1) and

Ir-P(2) bond lengths are very similar (~ 2.29 Å). As supported by the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopic data, the two phosphorus ligands are also situated in chemically identical environments with respect to the aryldiazenido ligand [P(1)-Ir-N(1) 91.4(2)°; P(2)-Ir-N(2) = 89.7(2)°]. Of specific interest in the structure of (2) is again the coordination mode and the orientation of the N_2Ar ligand. Unambiguously, the N_2Ar ligand has a doubly bent geometry with Ir-N(1)-N(2) and N(1)-N(2)-C(21) bond angles of 123.9(6)° and 117.1(8)°, respectively. The Ir-N(1) and N(1)-N(2) bond lengths of 2.028(7) Å and 1.210(10) Å are again as expected in comparison to other structurally determined doubly bent aryldiazenido compounds (Table 3). The stereochemistry about the N-N bond is trans and the dihedral angle between the planes defined by the *p*-methoxy phenyl ring and by N(1)-N(2)-C(21) is 15°. The corresponding angles in other doubly bent arydiazenido complexes range from 6° to 12°, all within a comparable range.[5] The coplanarity of the aryldiazenido ligand indicates extensive π conjugation including the *p*-methoxyphenyl ring and both nitrogens. Furthermore, unlike the singly bent N_2Ar case, the plane containing the N_2Ar group is pseudo-perpendicular to the Cp* plane, essentially bisecting the angle subtended by the two phosphorus groups. This is only the fourth reported X-ray crystal structure of a complex containing a doubly bent aryldiazenido ligand and the first for a "half sandwich" type structure.

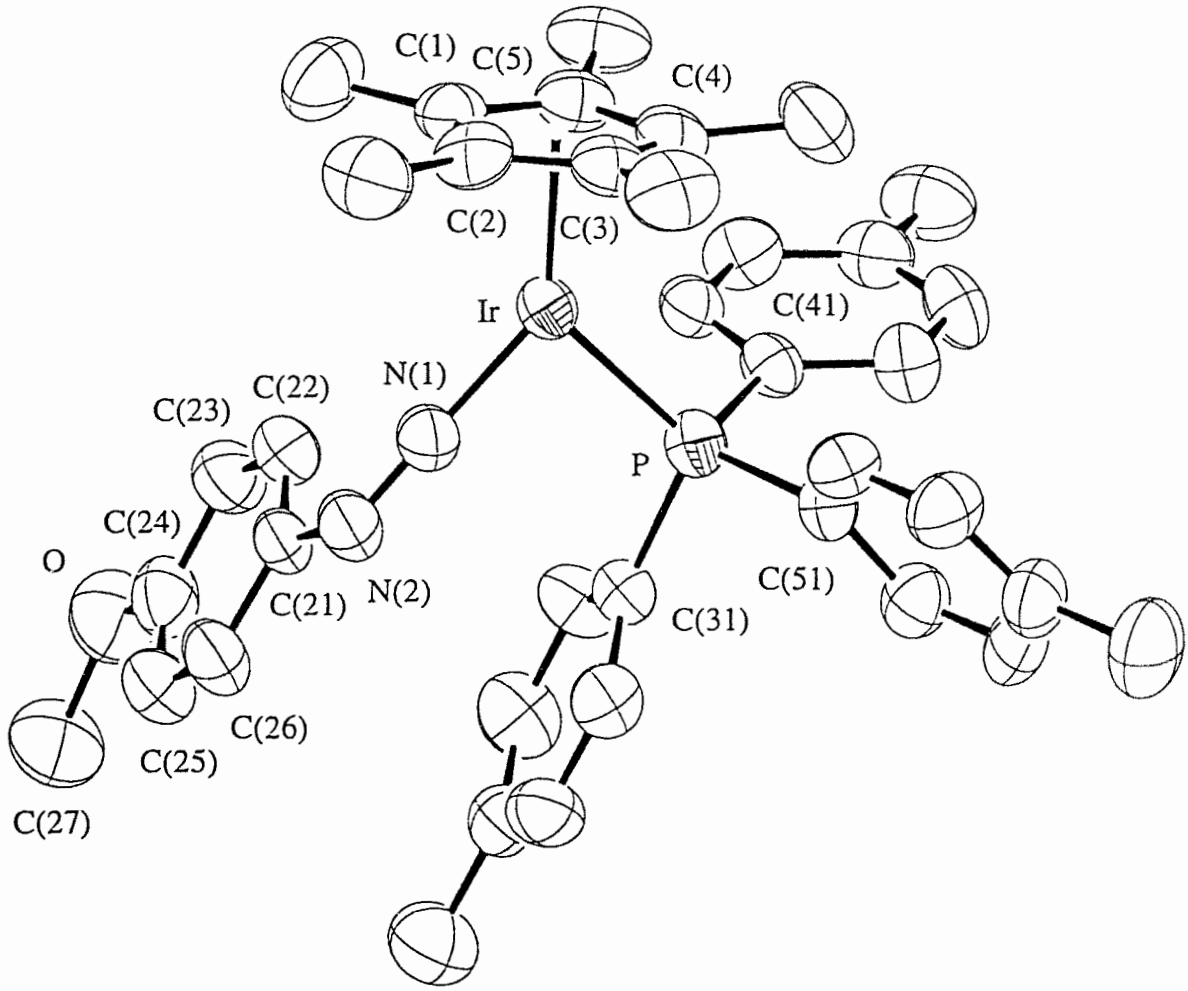


Fig. 12 Perspective view of the cation $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)]^+$

Table 6 Selected Distances, Angles and Torsion Angles[a] for $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)]^+$

Bond Distances (Å)

Ir-P	2.322(2)	Ir-C(1)	2.228(7)
Ir-N(1)	1.811(6)	Ir-C(2)	2.215(7)
N(1)-N(2)	1.205(8)	Ir-C(3)	2.263(7)
N(2)-C(21)	1.437(12)	Ir-C(4)	2.221(7)
O-C(24)	1.361(12)	Ir-C(5)	2.215(8)
O-C(27)	1.435(12)		

Bond Angles (°)[b]

P-Ir-Cp	132.5	N(1)-Ir-Cp	139.4
P-Ir-N(1)	87.9(2)	C(31)-P-C(41)	104.4(3)
Ir-P-C(31)	114.0(2)	C(31)-P-C(51)	102.8(3)
Ir-P-C(41)	112.2(2)	C(41)-P-C(51)	105.9(3)
Ir-P-C(51)	116.3(2)	N(2)-C(21)-C(22)	124.3(6)
Ir-N(1)-N(2)	177.7(6)	N(2)-C(21)-C(26)	116.4(7)
N(1)-N(2)-C(21)	120.2(7)	C(24)-O-C(27)	116.6(8)

Torsion Angles (°)

N(1)-Ir-P-C(31)	9.2(3)
N(1)-N(2)-C(21)-C(22)	–8.6(4)
N(1)-N(2)-C(21)-C(26)	167.7(10)
C(27)-O-C(24)-C(23)	175.1(10)
C(27)-O-C(24)-C(25)	–5.0(6)

[a] Values in parentheses are estimated standard deviations in the least significant figures.

[b] Cp represents the overall centre of mass of the C_5-ring.

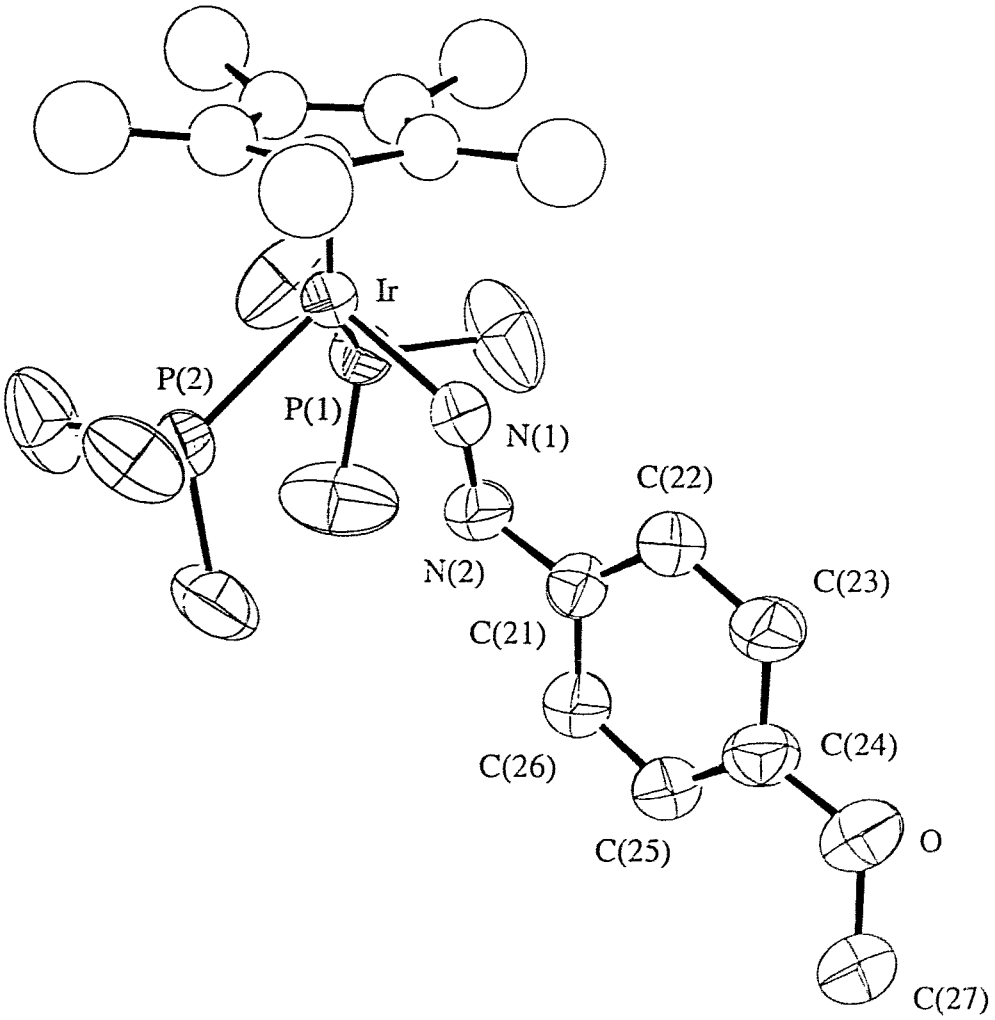


Fig. 13 Perspective view of the cation $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$

Table 7 Selected Distances, Angles and Torsion Angles[a] for $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$

Bond Distances (Å)

Ir-P(1)	2.292(2)	N(1)-N(2)	1.210(10)
Ir-P(2)	2.290(2)	N(2)-C(21)	1.440(11)
Ir-N(1)	2.028(7)	O-C(24)	1.371(11)
		O-C(27)	1.413(13)

Bond Angles (°)[b]

Cp-Ir-P(1)	126	Ir-N(1)-N(2)	123.9(6)
Cp-Ir-P(2)	126	N(1)-N(2)-C(21)	117.1(8)
Cp-Ir-N(1)	118	N(2)-C(21)-C(26)	116.2(8)
P(1)-Ir-P(2)	95.9(1)	N(2)-C(21)-C(22)	124.0(8)
P(1)-Ir-N(1)	91.4(2)	C(24)-O-C(27)	118.7(9)
P(2)-Ir-N(1)	89.7(2)		

Torsion Angles (°)

Ir-N(1)-N(2)-C(21)	−178.9(8)
N(1)-N(2)-C(21)-(26)	164.6(12)
N(1)-N(2)-C(21)-C(22)	−15.9(5)
C(27)-O-C(24)-C(23)	174.0(12)
C(27)-O-C(24)-C(25)	−6.5(7)
P(1)-Ir-N(1)-N(2)	−35.3(4)
P(2)-Ir-N(1)-N(2)	60.5(5)

[a] Values in parentheses are estimated standard deviations in the least significant figures.

[b] Cp represents the overall centre of mass of the C_5-ring.

CHAPTER III DISCUSSION

3.1 HISTORICAL BACKGROUND

The origin of the doubly bent aryldiazenido complex goes back to 1964 when Parshall first reported the platinum aryldiazenido complexes $[PtCl(PEt_3)_2(p\text{-}N_2C_6H_4Y)]$[24,25] (Y = F, H). Unlike the previously isolated singly bent aryldiazenido compounds, they exhibited lower NN stretches (1440–1463 cm^{-1}). In 1973, Ibers and Haymore then reported a synthetic route leading to a variety of new iridium aryldiazenido complexes, $[IrCl(X)(L)(PPh_3)_2(p\text{-}N_2C_6H_4Y)]$ where X = Cl, Br, I, N_3, NO_2, CNEt ; L = CO, EtNC; Y = F, H, which again showed low ν(NN) bands ranging from 1501–1461 cm^{-1}.[23] They proposed that in order for this six coordinate iridium complex to maintain an 18 electron system, the N_2Ar group must act as a one electron donor, *i.e.* be formally doubly bent N_2Ar^-. In the same year, Robinson, *et. al.* assigned their rhodium complex $[RhX_2(PPh_3)_2(N_2Ar)]$ (whose synthetic route and infrared spectroscopic data had been reported prior to the Ibers' and Haymore's iridium complex)[21,22] to also possess a doubly bent aryldiazenido ligand mainly basing their decision on its ν(NN) of *ca.* 1550–1615 cm^{-1}.[18] Up until this point, these assignments of a doubly bent coordination mode of the N_2Ar group in complexes were only tentative and no corroborating X-ray evidence existed.

Finally in 1973, Ibers, *et.al.* presented the first structural example of the doubly bent aryldiazenido compound for $[RhCl(PPP)(N_2Ph)]^+$.[15] This result confirmed the existence of doubly bent aryldiazenido compounds, but furthermore pointed out the inadequacy in using the NN stretching frequencies to differentiate singly bent and doubly bent aryldiazenido coordination modes in the complex. More specifically, their structurally determined rhodium doubly bent aryldiazenido complex showed relatively high NN bands (1627, 1561 cm^{-1}) that are well into the region usually assignable to singly bent aryldiazenido compounds. Nevertheless, other proposed doubly bent aryldiazenido compounds

$[IrCl(diphos)(N_2Ph)]^+$ and $[RhCl(diphos)(N_2Ph)]^+$ were presented, based upon infrared spectra with $\nu(NN)$ bands at *ca.* 1440-1493 cm^{-1}.[15] In 1975, Krogsrud and Ibers then confirmed, via X-ray crystal structure, the doubly bent geometry of the aryldiazenido ligand in the Parshall compound $[PtCl(PEt_3)_2(p\text{-}N_2C_6H_4F)]$, as has been previously suggested via IR.[4] Haymore and Ibers reported a few more doubly bent aryldiazenido compounds of type $[MX(CO)_2(PPh_3)_2(N_2Ph)]$ where M = Ru, Os, on the basis of $\nu(NN)$ = 1440–1458 cm^{-1} in the IR spectrum.[6] In 1977, Sutton, *et.al.*, then reported the X-ray crystal structure of $[IrCl_2(CO)(PPh_3)_2(o\text{-}N_2C_6H_4NO_2)]$,[5] confirming that the previously reported complex $[IrCl(X)(L)(PPh_3)_2(p\text{-}N_2C_6H_4Y)]$ by Ibers and Haymore indeed did possess a doubly bent N_2Ar ligand.

While infrared spectroscopy showed some deficiency in distinguishing between singly bent and doubly bent aryldiazenido compounds, it was the only spectroscopic method available for over ten years. In 1980, however, Richards, Mason, *et.al.*, discovered that the $^{15}N_\alpha$ resonance of aryldiazenido compounds in the ^{15}N NMR spectrum provides a rather clear and easy way of distinguishing the coordination mode of the aryldiazenido ligand.[33] For example, the $^{15}N_\alpha$ labelled rhodium complexes $[RhCl_2(PPh_3)_2(p\text{-}N_2C_6H_4Y)]$ exhibited N_α resonances which are dramatically downfield of nitromethane (δ 327 for Y = NO_2; δ 298 for Y = H), by comparison with the N_α resonance of singly bent aryldiazenido compounds which ranged from –28 to –56 ppm. In 1988, Mason, *et.al.*, undertook a more extensive investigation of the N_α chemical shifts for previously suggested doubly bent aryldiazenido compounds. They showed a definite distinction between the N_α resonances of singly and doubly bent aryldiazenido ligands observed by ^{15}N NMR.[20] For example, the structurally determined doubly bent aryldiazenido complexes $[PtCl(PEt_3)_2(p\text{-}N_2C_6H_4F)]$ and $[RhCl(PPP)(N_2Ph)]^+$ both showed very deshielded N_α chemical shifts of δ 285 and δ 138, respectively. Also, the N_α chemical shifts of $[IrCl_2(CO)(PPh_3)_2(N_2Ph)]$, a close analogue of the structurally determined complex $[IrCl_2(CO)(PPh_3)_2(o\text{-}N_2C_6H_4NO_2)]$, showed a dramatically deshielded N_α chemical shift of δ 241. In addition,

$[IrBr(diphos)(N_2Ph)]^+$ and $[RhCl(diphos)(N_2Ph)]^+$, the two compounds suggested by IR to have doubly bent aryldiazenido ligand, each displayed $^{15}N_\alpha$ resonances at δ 221 and at δ 225, corresponding well with the $^{15}N_\alpha$ chemical shifts observed for other doubly bent aryldiazenido compounds.

3.2 SYNTHETIC ROUTE

The doubly bent aryldiazenido complexes isolated to date seem to follow one of the following three synthetic routes;

(i) electrophilic attack of N_2Ar^+ at an electron-rich metal center (scheme 2)

(ii) deprotonation of the respective aryldiazene compound (scheme 3)

(iii) redistribution of electron density in a formal N_2Ar^+ complex through an additional ligand coordination (scheme 4)

There have been many doubly bent aryldiazenido compounds isolated by oxidatively adding a N_2Ar^+ ligand at an electron rich metal center. These compounds are usually prepared in one quick step either by simply introducing just the N_2Ar^+ ion to the compound, or by introducing N_2Ar^+ in presence of lithium halides. For example, the first structurally determined doubly bent arydiazenido complex $[Rh^{III}(PPP)Cl(N_2Ph)]^+$ was synthesized by oxidatively adding N_2Ph^+ to $[Rh^{I}(PPP)Cl]$.[15] Another structurally determined doubly bent aryldiazenido complex $[IrCl_2(PPh_3)_2(CO)(N_2Ar)]$ was synthesized by introducing a N_2Ar^+ solution containing LiCl to $[IrCl(CO)(PPh_3)_2]$.[5] Similarily, the rhodium complex $[RhX_2(PPh_3)_2(N_2Ar)]$ had been synthesized by reacting $[RhX(PPh_3)_3]$ with the aryldiazonium salt in the presence of lithium halides LiX (X = Cl or Br).[21,22]

On the other hand, there are not many examples of doubly bent aryldiazenido compounds that have been isolated according to the second synthetic route, *i.e.* deprotonation of the respective aryldiazene complex. The structurally determined doubly bent aryldiazenido compound $[PtCl(PEt_3)_2(N_2C_6H_5)]$[4] was synthesized by Parshall by deprotonating the platinum aryldiazene complex $[PtCl(PEt_3)_2(HNNPh)]^+$ [43] that had

been formed by reacting the platinum hydride $[PtHCl(PEt_3)_2]$ with an aryldiazonium salt. This synthetic route is well documented by the crystal structures of both the platinum aryldiazene "precursor" [43] as well as the deprotonated doubly bent aryldiazenido "product".[4] The infrared spectroscopically suggested doubly bent aryldiazenido compounds $[MH(CO)_2(PPh_3)_2(N_2Ph)]$ (M = Ru, Os) were also isolated in a similar manner to the platinum complex, *i.e.* by deprotonating the respective aryldiazene complexes $[MH(CO)_2(PPh_3)_2(HNNPh)]$.[6] Unfortunately, neither an X-ray crystal structure nor any ^{15}N NMR data to confirm the proposed doubly bent N_2Ar coordination mode is available for these ruthenium and osmium complexes.

When Haymore and Ibers reported the syntheses of the above hydrido doubly bent aryldiazenido complexes $[OsH(CO)_2(PPh_3)_2(N_2Ph)]$ and $[RuH(CO)_2(PPh_3)_2(N_2Ph)]$, they presented another synthetic route leading to doubly bent aryldiazenido compounds (scheme 4). This involved reacting the singly bent aryldiazendio complexes $[Os(CO)_2(PPh_3)_2(N_2Ph)]$ and $[Ru(CO)_2(PPh_3)_2(N_2Ph)]$ with coordinating anions to yield six-coordinate doubly bent aryldiazenido complexes.[6] Like the hydrido doubly bent ruthenium and osmium complexes, these compounds only have infrared spectroscopic evidence to support the proposed doubly bent coordination mode of the N_2Ar group. Therefore, the work in this thesis attempts to fully document this third synthetic route by obtaining the crystal structure, as well as the ^{15}N NMR data, on both the singly bent aryldiazenido precursor, as well as the formulated doubly bent aryldiazenido product.

3.3 NEW DOUBLY BENT ARYLDIAZENIDO COMPOUNDS

In order to unambiguously characterize the aryldiazenido coordination mode in the newly synthesized iridium complexes, ^{15}N NMR spectroscopy was utilized instead of infrared spectroscopy, since it has been proved to be a better method. Infrared spectrosopy was, however, used to assign the NN stretching frequency for the singly bent aryldiazenido compounds C and (1), and also as a method of monitoring reactions for (3) to (7) by

observing the disappearance of the ν(NN) bands due to the singly bent aryldiazenido compounds and the appearance of ν(CO) and ν(CN) bands for (6) and (7).

3.3.1 Iridium Singly Bent Aryldiazenido Precursor

In this work, the singly bent aryldiazenido compound $[Cp^*Ir(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$, where PR_3 = PPh_3, $P(p\text{-tol})_3$, was utilized to generate several new doubly bent aryldiazenido complexes. Since the singly bent aryldiazenido compound $[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C** had previously been shown to react with H^- to form a doubly bent aryldiazenido compound $[Cp^*Ir(PPh_3)H(p\text{-}N_2C_6H_4OMe)]$ **D** [δ ($^{15}N_\alpha$): 272 ppm], attempts were made to synthesize similar other singly bent aryldiazenido complexes of the type $[Cp^*Ir(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ with $P(p\text{-tol})_3$ and PMe_3 ligands, hoping to utilize them as a precursor to several other doubly bent aryldiazenido compounds

First, the singly bent aryldiazenido complex $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1) was successfully isolated by substituting the ethylene group in $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B** with $P(p\text{-tol})_3$. This substitution occurs rather readily since the strong π back bonding from Ir to the strong π acid (singly bent aryldiazenido) ligand induces lability of the ethylene ligand. The singly bent aryldiazenido compound (1) clearly showed ν(NN) at 1709 cm^{-1} (EtOH). As observed for **C**, ν(NN) of (1) occurs at a lower wavenumber than that exhibited by the starting complex $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B** (1709 cm^{-1}(1) vs 1724 cm^{-1} **B**). It was suggested that the better π acid character of the ethylene ligand compared with the phosphorus ligand provides less electron density at the metal center available for π back bonding to the antibonding π orbitals of the aryldiazenido ligand, resulting in higher value of ν(NN) for **B**.[37] Similarily, the deshielded N_α chemical shift of δ 33.7 in (1) compared with δ –2.26 in **B** from the ^{15}N NMR spectra is thought to be essentially caused by an increase in π back bonding. More specifically, the weaker π acid character of the phosphorus ligand in (1) decreases the energy gap between the highest occupied (HOMO) and the lowest

unoccupied (LUMO) molecular orbitals. This in turn increases the so called "non-spherical" electron density circulation (*i.e.* $\pi \leftrightarrow \pi^*$ transitions), essentially resulting in the relative downfield N_α chemical shift (Fig 14a).[44]

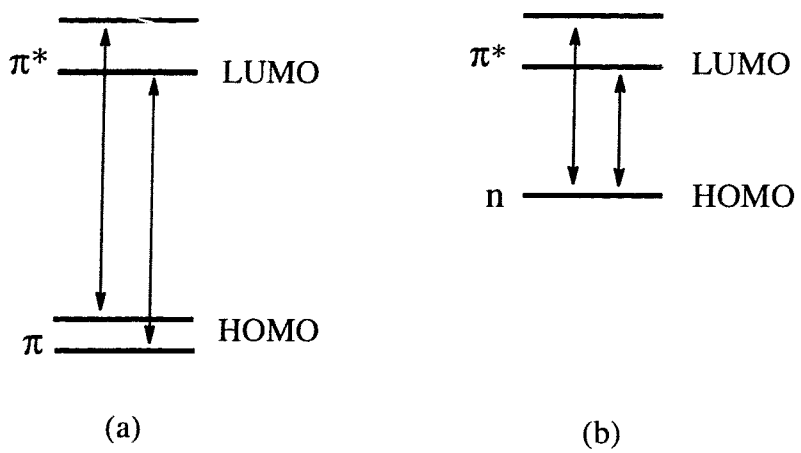


Fig. 14 (a) $\pi \leftrightarrow \pi^*$ and (b) $n \leftrightarrow \pi^*$ transitions at the N_2Ar group

As mentioned in chapter II, compound **C** was synthesized by reacting PPh_3 and $[p\text{-}N_2C_6H_4OMe]^+$ with $[Cp^*Ir(C_2H_4)_2]$ **A**. However, when the same synthetic route was utilized for (1), $[(p\text{-tol})_3P\text{–}(p\text{-}N_2C_6H_4OMe)]^+$ was inevitably produced as a by-product. This perhaps can be attributed to the difference in the basicity of the two phosphorus ligands. More specifically, the basic phosphorus atom center in $P(p\text{-tol})_3$ can act as another possible target for the electrophilic attack of $[p\text{-}N_2C_6H_4OMe]^+$ ligand to occur (other than the Ir metal center in **A**), finally yielding both $[(p\text{-tol})_3P\text{–}(p\text{-}N_2C_6H_4OMe)]^+$ and $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)]^+$. Formation of such a by-product is not surprising since the reaction of aryldiazonium ion with a nucleophilic center in a phosphorus ligand has often complicated the syntheses of several other aryldiazenido complexes. For example, the attempt to synthesize $[Fe(CO)_2(PPh_3)_2(p\text{-}N_2C_6H_4NEt_2)]^+$ from $Fe(CO)_3(PPh_3)_2$ and $[p\text{-}N_2C_6H_4NEt_2]^+$ resulted in a near quantitative amount of $[Ph_3P\text{–}(p\text{-}N_2C_6H_4NEt_2)]^+$.[45]

3.3.2 Systematic Isolation of Iridium Doubly Bent Aryldiazenido Compounds

While the reaction of $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)]^+$ with $P(p\text{-tol})_3$ yielded the expected singly bent aryldiazenido complex, the similar attempt with PMe_3 was much more rewarding, providing us with the doubly bent aryldiazenido complex $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2). Isolation of $[Cp^*Ir(PMe_3)(p\text{-}N_2C_6H_4OMe)]^+$ perhaps never succeeded due to facile coordination of two equivalents of PMe_3, stimulated by the excess amount of PMe_3 present in the system. We hypothesize that initially one equivalent of PMe_3 coordinates to the metal center forming a singly bent cationic species; then, the sequential attack at the electron-deficient metal center by another equivalent of PMe_3 results in the doubly bent aryldiazenido compound.

In order to support this proposed synthetic scheme for isolating doubly bent aryldiazenido compounds, various phosphorus ligands such as PMe_3, PPh_3 or $P(p\text{-tol})_3$ were introduced to the monophosphine singly bent aryldiazenido compounds $[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C** or $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1). As expected, PMe_3 was successfully coordinated to both **C** and (1) yielding $[Cp^*Ir(PPh_3)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (3) and $[Cp^*Ir\{P(p\text{-tol})_3\}(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (4). This clearly demonstrates cases in which the singly bent aryldiazenido ligand isomerizes to give the doubly bent aryldiazenido compound due to addition of an electron pair donor to the metal. Furthermore, it supports our proposed synthetic route for (1), even though the initial formation of a singly bent aryldiazenido complex $[Cp^*Ir(PMe_3)(p\text{-}N_2C_6H_4OMe)]^+$ was never observed.

While two equivalents of PMe_3 easily coordinated to the metal center forming a doubly bent aryldiazenido complex $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2), attempts to synthesize analogous compounds with two equivalents of PPh_3 and $P(p\text{-tol})_3$ did not succeed. Coordination of the bidentate ligand, $Ph_2PC_2H_4PPh_2$ (diphos) to $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B**, however, was successful. This suggests that the inability to synthesize $[Cp^*Ir(PPh_3)_2(p\text{-}N_2C_6H_4OMe)]^+$ or $[Cp^*Ir\{P(p\text{-tol})_3\}_2(p\text{-}N_2C_6H_4OMe)]^+$

probably is due to it being a sterically hindered process, since the less sterically demanding diphos can coordinate both phosphorus atoms. The possibility of these reactions being electronically unfavoured because of the π acceptor nature of the phosphines is highly improbable in view of the success with diphos and since some strong π electron withdrawing ligands such as CO, CN were successfully coordinated to $[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C** to yield the respective doubly bent aryldiazenido complexes $[Cp^*Ir(PPh_3)(CO)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (6) and $[Cp^*Ir(PPh_3)(CN)(p\text{-}N_2C_6H_4OMe)]$ (7) (see below).

As depicted in Table 5, introducing a second ancillary ligand to the singly bent aryldiazenido system causes more than a 200 ppm downfield chemical shift of the N_α resonance, clearly indicating the formation of a doubly bent aryldiazenido ligand in the resulting complexes. The dramatic deshielding in N_α is considered to be due to the presence of a lone pair on the N_α nitrogen in the doubly bent N_2Ar case. This non-bonding electron density on the N_α nitrogen increases the $n(N) \leftrightarrow \pi^*$ electron density circulation, thus resulting the dramatic downfield shift of the N_α resonance (Fig 14b).[44]

Another spectroscopic feature observed upon converting the singly bent to the doubly bent aryldiazenido compounds is the disappearance of the ^{31}P-^{15}N coupling observed in the $^{31}P\{^1H\}$ and ^{15}N NMR spectra of the latter. While ^{31}P-^{15}N coupling is easily observed in the singly bent aryldiazenido complexes **C** and (1) [$J_{^{31}P\text{-}^{15}N}$ = 6 to 7 Hz] where the phosphorus ligand and the N_2Ar ligand are pseudo-trans to each other in a two legged piano stool structure, no measureable ^{31}P-^{15}N coupling is observed for the three legged piano stool, doubly bent aryldiazenido complexes (2)-(7) that have the phosphorus groups in mutual cis positions. However, the $^{31}P\{^1H\}$ NMR spectra of (3) and (4) did clearly show ^{31}P–^{31}P coupling between the two inequivalent cis phosphorus ligands present. Some of the other reported doubly bent aryldiazenido complexes like $[Os(X)(CO)_2(PPh_3)_2(N_2Ph)]^+$ [6] and $[Cp^*Ir(H)(PPh_3)(p\text{-}N_2C_6H_4OMe)]$ [26] have also displayed the absence of the ^{31}P-^{15}N couplings in the $^{31}P\{^1H\}$ or ^{15}N NMR spectra.

3.3.3 Other Co-Ligands Which Favour Singly Bent - Doubly Bent N_2Ar Conversion

Having isolated several new bisphosphine doubly bent aryldiazenido systems, attempts were made to establish the trend of ligands that could induce stereochemical transformation in the singly bent system as well as stabilize the doubly bent aryldiazenido complexes so produced. While coordination of weak π acid ligands, PR_3, to the singly bent aryldiazenido complex $[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C** was achieved under mild conditions (*i.e.* room temperature), attempts to coordinate hydride or π base ligand, Cl^-, had been shown to be not as facile; *i.e.*, the previously isolated compounds $[Cp^*Ir(PPh_3)(H)(p\text{-}N_2C_6H_4OMe)]$ **D** required low temperature and the compound $[Cp^*Ir(PPh_3)(Cl)(p\text{-}N_2C_6H_4OMe)]$ could not be observed.[37] Successful coordination of CO and CN^- ligands to **C**, if it occurred, might indicate that perhaps ligands with π acid character are preferred as the second incoming ancillary ligand for stabilizing the doubly bent aryldiazenido ligand in the system of general formula $[Cp^*Ir(PR_3)(L_2)(p\text{-}N_2C_6H_4OMe)]^{+,0}$.

As in the case of (3)–(5), introducing CO and CN^- to the singly bent aryldiazenido compounds was observed to cause a dramatic downfield shift in the $^{15}N_\alpha$ resonance, strongly implying that coordination had occurred and that a doubly bent N_2Ar group had resulted in (6) and (7). For (6), the infrared spectrum showed a band corresponding to $\nu(CO)$ at 2039 cm^{-1} (EtOH). It is significantly lower than other reported $\nu(CO)$ values (in the region of 2060 cm^{-1}) for the iridium (III) doubly bent aryldiazenido complexes of general formula $[IrCl_2(CO)(PPh_3)_2(p\text{-}N_2C_6H_4R)]$ (R = H, F, Br, NO_2, OMe). Probably the very good electron donating Cp* group in (6) provides the formal Ir(III) metal center with sufficient electron density to allow more $\pi \rightarrow \pi^*$ back donation to the CO ligand, resulting in the low $\nu(CO)$ value. The $\nu(CN)$ value of 2108 cm^{-1} for (7) is in the expected region, *i.e.* at a higher wavenumber than that for $\nu(CO)$. In aqueous solution, the $\nu(CN)$ of free CN^- is 2080 cm^{-1} and the corresponding wavenumber for free CO is 2143 cm^{-1}. However, the better σ-donating and a poorer π-accepting characteristic of CN compared with CO

results in higher ν(CN) for cyano complexes (2200-2000 cm^{-1}) than ν(CO) values for carbonyl complexes (2105-1850 cm^{-1}).[46] Unfortunately, no other known cyano doubly bent aryldiazenido complexes exist for exact comparison.

3.4 X-RAY CRYSTAL STRUCTURES

An attempt has been made to fully document the resulting transformation of a singly bent to a doubly bent aryldiazenido compound by using X-ray crystallography. This can be achieved by evaluating the X-ray crystal structures of the singly bent aryldiazenido precursor and the transformed doubly bent aryldiazenido product. While this has not been fully accomplished, in the sense of the before and after addition of PR_3 to the same aryldiazenido complex, two crystal structures representing the monophosphine singly bent aryldiazenido compound (1) [PR_3 = P(*p*-tol)$_3$] and the bisphosphine doubly bent aryldiazenido compound (2) [PR_3 = PMe_3] have been determined.

The X-ray crystal structure determination for (1) was carried out to mainly identify the geometry of the coordinated aryldiazenido group. A comparison of the bond distances and angles of the aryldiazenido ligand in (1) has been made in Table 8 with two other iridium singly bent aryldiazenido complexes.[34,47] As expected, the structural dimensions exhibited by **B** and (1) are almost identical and are also in good agreement with other reported values.[48] Another structural feature observed in both of the singly bent aryldiazenido compounds **B** and (1) is the orientation of the aryldiazenido group. The N(1), N(2), aromatic, and methoxy oxygen atoms are essentially coplanar, and the N_2Ar plane is situated pseudo-parallel to the Cp* plane (Fig. 15a). The reported Ir-P bond lengths in the literature vary significantly depending on the number and type of ligands present and their disposition (*i.e.*, from 2.287 Å to 2.403 Å)[47,49], thus it is difficult to draw exact comparison. Nevertheless, the value obtained for (1) is well within the range of the other Ir-P bond distances.

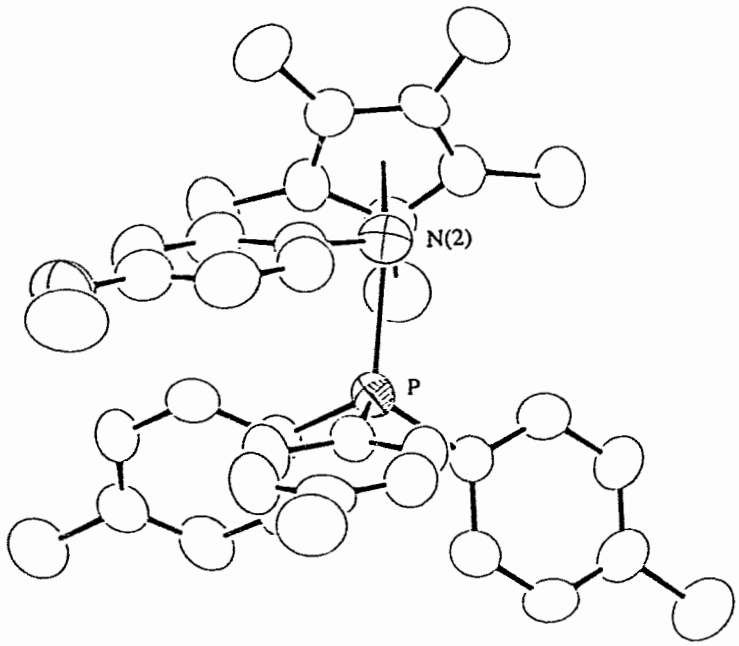
Table 8 Selected Bond Distances(Å) and Angles(°) for Iridium Singly Bent Aryldiazenido complexes

Parameters	$[Cp^*Ir\{P(p\text{-tol})_3\}(N_2Ar)]^+$	$[Cp^*Ir(C_2H_4)(N_2Ar)]^{+a}$	$[IrCl(PPh_3)_2(N_2Ph)]^{+b}$
Ir-N(1)	1.811(6)	1.811(7)	1.800(10)
N(1)-N(2)	1.205(8)	1.205(9)	1.163(11)
Ir-P	2.322(2)	———	2.350(2); 2.339(2)
Ir-N(1)-N(2)	177.7(6)	176.2(6)	175.8(8)
N(1)-N(2)-C(21)	120.2(7)	120.4(6)	126.9(10)

[a] Ref. 34 [b] Ref. 47 [c] Ar = (p-C_6H_4OMe)

The crystal structure of (2) exemplifies the doubly bent aryldiazenido compounds in this work. As mentioned earlier, the X-ray crystal structure for (2) is only the fourth reported example of a doubly bent aryldiazenido compound, but more importantly, it is the first example among those that exhibit a "half sandwich" structure. In previously determined X-ray crystal structures, the five-coordinate rhodium complex $[RhCl(PPP)(N_2Ph)]^+$ possesses square pyramidal geometry with the aryldiazenido group occupying the apical coordination site, the geometry of the four-coordinate complex $[PtCl(PEt_3)_2(p\text{-}N_2C_6H_4F)]$ is square planar with trans phosphine ligands, and finally, the doubly bent aryldiazenido ligand in $[IrCl_2(CO)(PPh_3)_2(o\text{-}N_2C_6H_4NO_2)]$ is present in a six-coordinate iridium complex (Fig. 16). Table 9 compares some selected dimensions in all four doubly bent aryldiazenido complexes. Clearly, there is no significant deviation in the values obtained for (2) compared with other doubly bent aryldiazenido complexes. The doubly bent N_2Ar ligand is known to have a large trans lengthening influence on its trans ancillary ligand. For example in the iridium complex, the trans chloride ligand Ir-Cl(2) has a distance of 2.48(1) Å, while the cis Ir-Cl(1) bond distance is 2.37(1) Å. Similarly, in the platinum complex, a rather long Pt-Cl bond distance of 2.413(6) Å was observed for the chloride ligand trans to the N_2Ar ligand (Fig. 16). On the other hand, the site trans to the aryldiazenido ligand in both the rhodium complex $[RhCl(PPP)(N_2Ph)]^+$ or (2) is unoccupied (Figs. 13, 16). Thus, no trans lengthening influence could be observed .

(a) $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)]^+$ (view along Ir-N(1)-N(2) bond)



(b) $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$ (view along Ir-N_2Ar plane)

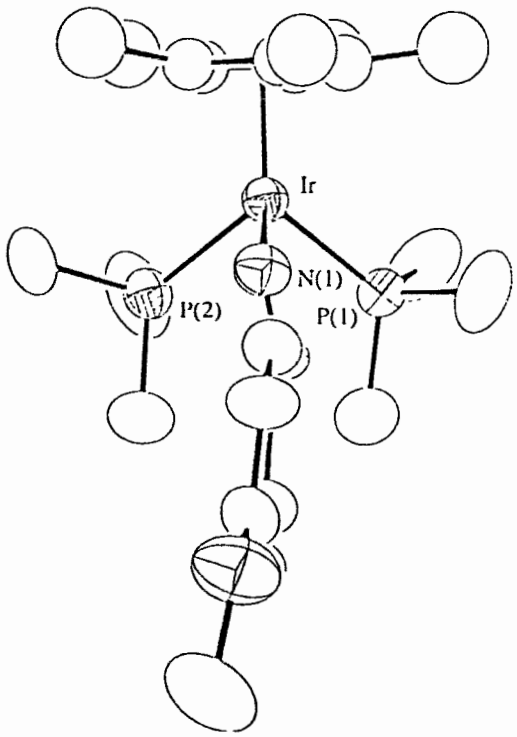
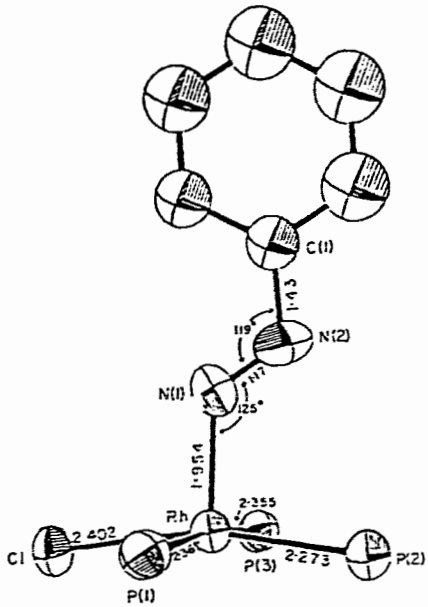
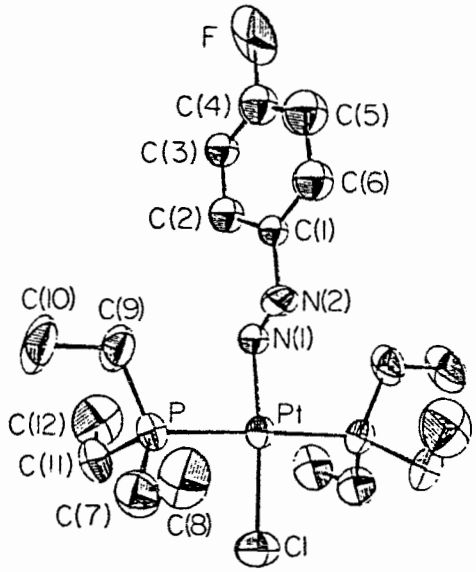


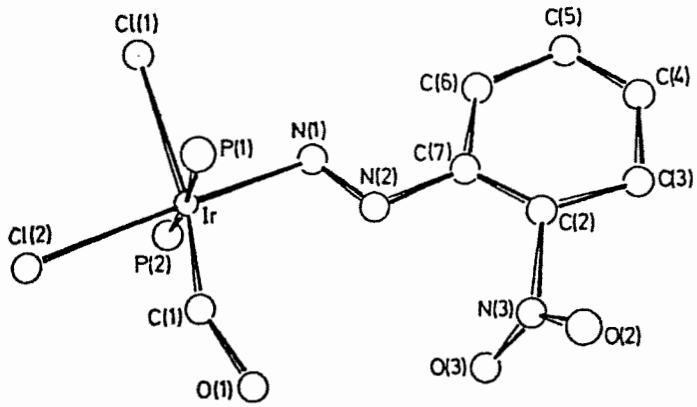
Fig. 15 N_2Ar ligand orientation in (a) $[Cp^*Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)]^+$ and (b) $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$



(a) $[RhCl(PPP)(N_2Ph)]^+$



(b) $PtCl(PEt_3)_2(p\text{-}N_2C_6H_4F)$



(c) $IrCl_2(CO)(PPh_3)_2$ $(o\text{-}N_2C_6H_4NO_2)$

Fig. 16 Molecular structures of doubly bent aryldiazenido compounds

Table 9 Selected Bond Distances(Å) and Angles(°) for Doubly Bent Aryldiazenido Complexes

Complex	M-N (Å)	N-N (Å)	M-P (Å)	M-N-N (°)	N-N-C (°)
$[Cp^*Ir(PMe_3)_2(N_2C_6H_4OMe)]^+$	2.028(7)	1.210(10)	2.292(2); 2.290(2)	123.9(6)	117.1(8)
$IrCl_2(CO)(PPh_3)_2(o\text{-}N_2C_6H_4NO_2)$	2.05(4)	1.19(4)	2.37(1)	115(3)	115(3)
$PtCl(PEt_3)_2(p\text{-}N_2C_6H_4F)$	1.97(3)	1.17(3)	2.302(4)	118(2)	118(2)
$[RhCl(PPP)(N_2Ph)]^+$	1.961(7)	1.172(9)	2.274(3) – 2.368(3)	125.1(6)	118.9(8)

While there have been many comparisons and discussions on the different bond distances and angles exhibited by the singly and doubly bent aryldiazenido ligand in their complexes, no particular attention has been paid to the difference in the orientation of the aryldiazenido ligand in these two geometries. In fact, such a difference was not readily apparent, since no related pairs of structurally determined singly and doubly bent aryldiazenido complexes in a comparable system existed before. Only one indirect correlation has been made by comparing the singly bent aryldiazenido compound $[(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ [48,50] with the hydrazido(2–) compound $[(\eta^5\text{-}C_5H_5)Re(CO)_2\{NN(Me)C_6H_4OMe\}]$[51], where it is proposed that, in order to establish a better overlap of the filled metal d orbital and the empty π^* orbital of the N_2Ar ligand, the transformation of a singly bent to a doubly bent aryldiazenido ligand is accompanied by a 90° ligand rotation about the $M\text{-}N_\alpha$ bond.[37] We now have obtained crystal structures of both singly and doubly bent aryldiazenido complexes that are in a very similar system, which in turn allows us to draw a valid comparison regarding the orientation of the aryldiazenido ligand in the two geometries. As has been indicated above, while the plane defined by the aryldiazenido ligand in (1) is pseudo-parallel to the Cp* plane, the same plane in (2) is perpendicular to the Cp* plane, indicating that the singly bent to doubly bent transformation is indeed accompanied by a 90° ligand rotation about the Ir-N(1) bond (Fig. 15).

3.5 CONCLUSION

In this work, one phosphorus ligand has been introduced to $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)]^+$ to yield a monophosphine singly bent aryldiazenido compound (1). Subsequently, addition of two phosphorus ligands has been shown to provide bisphosphine doubly bent aryldiazenido compounds (2)-(4). Using ^{15}N NMR spectroscopy, the systematic conversion of a singly bent aryldiazenido compound to a doubly bent aryldiazenido compound has been successfully documented. More importantly, the crystal structures of a monophosphine singly bent and a bisphosphine doubly bent aryldiazenido complex that share a similar overall geometry (*i.e.* piano stool structure) have been determined, fully documenting the structural results of this transformation process. This novel accomplishment also enabled us to compare the simple dimensional characters of these aryldiazenido ligands such as bond distances and angles. Furthermore, a clear distinction in the $M\text{-}N_2Ar$ orientation in these two geometries has been observed. Finally, we proposed that the stabilization of the doubly bent aryldiazenido ligand in the system of general formula $[Cp^*Ir(PR_3)(L)(p\text{-}N_2C_6H_4OMe)]^{+,0}$ is enhanced when the second ancillary ligand, L, exhibits some π acid character.

CHAPTER IV EXPERIMENTAL

4.1 GENERAL PROCEDURES

All solvents were dried and purified by standard methods and were freshly distilled under nitrogen immediately before use. All reactions and manipulations were carried out in standard Schlenk ware, connected to a switchable double manifold providing vacuum and nitrogen. These reactions were performed at room temperature, unless otherwise mentioned. Infrared spectra were measured for solutions in CaF_2 cells by using a Bomem Michelson 120 FTIR instrument. The routine ^1H NMR spectra were recorded at 100 MHz by using a Bruker SY-100 Fourier Transform Spectrometer. Chemical shifts (δ) are reported in ppm, downfield positive, relative to tetramethylsilane (TMS). ^{15}N NMR and ^{31}P NMR were obtained by Mrs. M. M. Tracey of the NMR service of Simon Fraser University on a Bruker AMX-400 Fourier Transform instrument at operating frequencies of 40.5 MHz and 162 MHz for ^{15}N and ^{31}P, respectively. Chemical shifts (ppm) are reported (downfield positive) with respect to external references of $MeNO_2$ for ^{15}N and 85% H_3PO_4 for ^{31}P. Fast atom bombardment (FAB) or electron impact (EI) mass spectra were obtained by Mr. G. L. Owen on a Hewlett-Packard Model 5985 spectrometer equipped with a fast atom bombardment probe (xenon source, Phrasor Scientific, Inc., accessory). Samples for FABMS were dissolved in *m*-nitrobenzyl alcohol (NOBA). The observed isotope patterns of the parent and fragment ions are reported based on the more abundant isotope, *i.e.* ^{193}Ir. Microanalyses were performed by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University. The melting points were obtained using Fisher-Johns melting point apparatus and are uncorrected.

The *p*-methoxybenzenediazonium tetrafluoroborate was prepared by the standard procedure using *p*-anisidine (Aldrich) and sodium nitrite. It was recrystallized periodically from acetone and diethyl ether. The $^{15}N_\alpha$ labelled salt [*p*-$^{15}NNC_6H_4OMe$][BF_4] was

prepared from $Na^{15}NO_2$ (95% ^{15}N enriched, MSD isotope) and was employed for the syntheses of ^{15}N labelled compounds.

4.2 SYNTHESES

4.2.1 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ C

To a 10 mL ethanol solution containing equimolar quantities of $Cp^*Ir(C_2H_4)_2$ **A** (30 mg, 0.078 mmol) and PPh_3 (20 mg, 0.078 mmol), $[p\text{-}N_2C_6H_4OMe][BF_4]$ (17 mg, 0.078 mmol) was added. Upon introducing the diazonium salt, the colorless solution immediately changed to orange red. The reaction mixture was stirred for 1 hour, and was vacuum dried to give an orange-red oil. IR ν(NN): 1701 cm^{-1} (EtOH), ν(^{15}NN): 1676 cm^{-1} (EtOH); ^1H NMR (294K, 100 MHz, acetone-d_6): δ 2.03 (d, $J_{P\text{-}H}$ = 2 Hz, 15H, Cp*), 3.85 (s, 3H, $p\text{-}C_6H_4OMe$), 6.95 (d, 2H, $p\text{-}C_6H_4OMe$), 7.15 (d, 2H, $p\text{-}C_6H_4OMe$), 7.46–7.75 (m, 15H, PPh_3); $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 9.57 (d, $J_{P\text{-}^{15}N\alpha}$ = 7 Hz, PPh_3); ^{15}N NMR (40.5 MHz, acetone-d_6): δ 33.23 (d, $J_{P\text{-}^{15}N\alpha}$ = 7 Hz, $^{15}N_\alpha$); FABMS (NOBA, xenon): m/z 725 (M^+), 590 ($M^+ - N_2C_6H_4OMe$); Anal. Calcd: C, 51.79 ; H, 4.60; N, 3.45. Found: C, 52.18 ; H, 4.81 ; N, 3.62.

4.2.2 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1)

$Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B** (30 mg; 0.052 mmol) in acetone (5 mL) was stirred with equimolar $P(p\text{-tol})_3$ (16 mg: 0.052 mmol) at 0 °C for 15 min. The reaction mixture immediately changed color from yellow to orange. Excess hexane was then added while stirring until no further precipitation occurred. Recrystallization from acetone/hexane (1 : 5; volume/volume) at −10 °C gave orange crystals suitable for X-ray crystal analysis (35 mg, 0.041mmol, 79%). IR ν(NN): 1709 cm^{-1} (EtOH), ν(^{15}NN): 1674 cm^{-1} (EtOH); ^1H NMR (294K, 100 MHz, acetone-d_6): δ 2.04 (d, $J_{P\text{-}H}$ = 2 Hz, 15H, Cp*), 2.35 (s, 9H, $p\text{-}C_6H_4Me$), 3.86 (s, 3H, $p\text{-}C_6H_4OMe$), 6.94 (d, 2H, $p\text{-}C_6H_4OMe$), 7.10 (d, 2H, $p\text{-}C_6H_4OMe$), 7.23–7.42 (m, 12H, $p\text{-}C_6H_4Me$); $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6):

δ 7.48 (d, J_{P-15N_α} = 6 Hz, P(*p*-tol)$_3$); ^{15}N NMR (40.5 MHz, acetone-d$_6$): δ 33.68 (d, J_{P-15N_α} = 6 Hz, $^{15}N_\alpha$); FABMS (NOBA, xenon): m/z 767 (M^+), 631 (M^+ – $N_2C_6H_4OMe$, H), 461 (M^+ – P(*p*-tol)$_3$, 2H) ; Anal. Calcd: C, 53.45; H, 5.09; N, 3.28. Found: C, 53.51; H, 5.38 ; N, 2.93; Melting Point: 120-125 °C dec.

4.2.3 Reaction of P(*p*-tol)$_3$ with [*p*-$N_2C_6H_4OMe$][BF_4]

Tri-*p*-tolylphosphine (5 mg; 0.016 mmol) in acetone-d$_6$ (3 mL) and equimolar [*p*-$N_2C_6H_4OMe$][BF_4] (3.7 mg; 0.016 mmol) were mixed and stirred for 5 min. The colorless solution immediately changed to orange. ^{1}H NMR (294K, 100 MHz, acetone-d$_6$): δ 2.54 (s, 9H, *p*-C_6H_4*Me*), 4.03 (s, 3H, *p*-C_6H_4O*Me*), 7.26 (d, 2H, *p*-C_6*H*$_4$OMe), 8.15 (d, 2H, *p*-C_6*H*$_4$OMe), 7.59 – 7.90 (m, 12H, *p*-C_6*H*$_4$Me).

4.2.4 Preparation of [(η^5-C_5Me_5)Ir(PMe_3)$_2$(*p*-$N_2C_6H_4OMe$)][BF_4] (2)

To an acetone solution (5 mL) containing [Cp*Ir(C_2H_4)(*p*-$N_2C_6H_4OMe$)][BF_4] **B** (30 mg; 0.052 mmol), 0.1 mL of prediluted PMe_3 was added. (Pre-diluted PMe_3 was prepared in a separate Schlenk tube by thoroughly mixing 0.03 mL of PMe_3 with 3 mL acetone just before use.) The solution immediately changed color from yellow to yellowish orange. The reaction mixture was stirred for 15 min. Excess hexane was then added while stirring in order to precipiate the orange solid. Recrystallization of (2) from acetone/hexane (1 : 5) at –10 °C gave reddish orange crystals (thin needles) suitable for X-ray analysis. (29 mg, 0.04 mmol, 80%). ^{1}H NMR (100MHz, acetone-d$_6$): δ 1.66 (d, J_{P-H} = 10 Hz, 18H, PMe_3), 1.86 (t, J_{P-H} = 2 Hz, 15H, Cp*), 3.82 (s, 3H, *p*-C_6H_4O*Me*), 6.98 (d, 2H, *p*-C_6*H*$_4$OMe), 7.40 (d, 2H, *p*-C_6*H*$_4$OMe); ^{31}P{^{1}H} NMR (162 MHz, acetone-d$_6$): δ –37.73 (s, PMe_3); ^{15}N NMR (40.5 MHz, acetone-d$_6$): δ 243.1 (s, $^{15}N_\alpha$); FABMS (NOBA, xenon): m/z 615 (M^+), 539 (M^+ – PMe_3), 480 (M^+ – $N_2C_6H_4OMe$), 463 (M^+ – 2 PMe_3); Anal. Calcd: C, 39.37; H, 5.76 ; N,3.99. Found: C, 39.24; H, 5.73; N, 3.97; Melting Point: 143-146 °C dec.

4.2.5 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (3)

To $[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C** (50 mg; 0.062 mmol) in ethanol (5 mL), 0.1 mL of pre-diluted PMe_3 was added using a syringe. PMe_3 was pre-diluted in the same way described in the synthesis of (2), but with ethanol solvent. The reaction mixture was stirred (*ca.* 15 min) until the ν(NN) stretch from compound **C** disappeared as monitored by IR. The solution remained orange and no obvious color change was observed throughout the reaction. Excess hexane was then added while stirring in order to precipiate the desired product. Recrystallization from acetone/hexane (1 : 5) at room temperature gave yellowish orange solid in 94 % yield (51 mg, 0.058 mmol). ^1H NMR (294K, 100 MHz, acetone-d_6): δ 1.24 (d, $J_{P\text{-}H}$ = 11 Hz, 9H, PMe_3), 1.47 (t, $J_{P\text{-}H}$ = 3 Hz, 15H, Cp*), 3.84 (s, 3H, $p\text{-}C_6H_4OMe$), 7.00 (d, 2H, $p\text{-}C_6H_4OMe$), 7.39 (d, 2H, $p\text{-}C_6H_4OMe$), 7.45–7.82 (m, 15H, PPh_3); $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ −3.31 (d, $J_{P\text{-}P}$ = 21 Hz, PPh_3), −36.20 (d, $J_{P\text{-}P}$ = 21 Hz, PMe_3); ^{15}N NMR (40.5 MHz, acetone-d_6): δ 234.1 (s, $^{15}N_\alpha$); FABMS (NOBA, xenon): m/z 801 (M^+), 725 ($M^+ - PMe_3$), 666 ($M^+ - N_2C_6H_4OMe$), 539 ($M^+ - PPh_3$); Anal. Calcd for (3): C, 51.40; H, 5.23; N, 3.16. Anal. Calcd for (3)·H_2O: C, 50.38; H, 5.35; N, 3.09. Found: C, 50.44; H, 5.56; N, 3.06; Melting Point: 112-116 °C dec.

4.2.6 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir\{P(p\text{-tol})_3\}(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (4)

0.1 mL of pre-diluted PMe_3 in acetone (see section 4.2.4) was directly added to $[(\eta^5\text{-}C_5Me_5)Ir\{P(p\text{-tol})_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1) (40 mg; 0.047 mmol) to give an yellowish orange solution. The reaction mixture was stirred until ν(NN) at 1709 cm^{-1} (EtOH) from compound (1) disappeared (as monitored by IR). Excess hexane was added to precipitate the crude product. Recrystallization from acetone/hexane (1 : 5) at room temperature gave orange solid in 93 % yield. (41 mg, 0.044 mmol). ^1H NMR (294K, 100 MHz, acetone-d_6): δ 1.23 (d, $J_{P\text{-}H}$ = 11 Hz, 9H, PMe_3), 1.46 (t, $J_{P\text{-}H}$ = 2 Hz, 15H, Cp*), 2.39 (s, 9H, $p\text{-}C_6H_4Me$), 3.84 (s, 3H, $p\text{-}C_6H_4OMe$), 7.02 (d, 2H, $p\text{-}C_6H_4OMe$),

7.25–7.46 (m, 2H, p-C_6H_4OMe), 7.25–7.46 (m, 12H, p-C_6H_4Me); $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ −5.39 (d, J_{P-P} = 23 Hz, P(p-tol)$_3$), δ −36.03 (d, J_{P-P} = 23 Hz, PMe_3); ^{15}N NMR (40.5 MHz, acetone-d_6): δ 236.1 (s, $^{15}N_\alpha$); FABMS (NOBA, xenon): m/z 708 (M^+ – $N_2C_6H_4OMe$), 631 (M^+ – $N_2C_6H_4OMe$, PMe_3), 539 (M^+ – P(p-tol)$_3$); Anal. Calcd: C, 52.95; H, 5.65; N, 3.01 Found: C, 52.75; H, 5.96; N, 3.00; Melting Point: 125-128 °C dec.

4.2.7 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(Ph_2PC_2H_4PPh_2)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (5)

To $[Cp^*Ir(C_2H_4)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **B** (30 mg; 0.052 mmol) in acetone (5 mL), an equimolar $Ph_2PC_2H_4PPh_2$ (diphos) (21 mg; 0.052 mmol) was added and the mixture was stirred for 15 min. An immediate color change from yellow to yellowish orange was observed. The loss of ν(NN) absoprtion at 1724 cm^{-1} in ethanol confirmed completion of the reaction. Excess hexane was added while stirring in order to precipitate the desired product. Recrystallization from acetone/hexane (1 : 5) at room temperature yielded a yellowish orange powder in 97 % yield (48 mg, 0.050 mmol). ^1H NMR (294K, 100 MHz, acetone-d_6): 1.54 (t, J_{P-H} = 2 Hz, 15H, Cp*), 3.69 (s, 3H, p-C_6H_4O*Me*), 6.41 (d, 2H, p-C_6H_4OMe), 6.66 (d, 2H, p-C_6H_4OMe), 7.38–7.86 (m, 20 H, PPh_3); $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 43.84 (s, PPh_3); ^{15}N NMR (40.5 MHz, acetone-d_6): δ 229.0 (s, $^{15}N_\alpha$) ; FABMS (NOBA, xenon): m/z 726 (M^+ – $N_2C_6H_4OMe$), 461 (M^+ – diphos, 2H) ; Anal. Calcd: C, 54.48 ; H, 4.90 ; N, 2.96 Found: C, 54.56 ; H, 5.04 : N, 2.70; Melting Point: 164-169 °C dec.

4.2.8 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(CO)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (6)

Carbon monoxide (c.p. grade) was bubbled briefly (2-3 min) through an ethanol solution (5 mL) of **C** (50 mg; 0.062 mmol). The reaction mixture was stirred for 30 min. The color change from orange to yellowish orange was observed. The reaction proceeded with the disappearance of ν(NN) bands at 1701 cm^{-1} (EtOH) and concurrent production of

a ν(CO) band at 2039 cm^{-1} (EtOH). Excess hexane was added to precipitate the crude product. Recrystallization from ethanol/hexane (1 : 5) gave a yellowish orange powder (50 mg, 0.059 mmol, 95 %). IR ν(CO) 2039 cm^{-1} (EtOH); ^1H NMR (294K, 100 MHz, acetone-d_6): 1.78 (d, J_{P-H} = 3 Hz, 15H, Cp*), 3.82 (s, 3H, *p*-C_6H_4OMe), 6.91 (d, 2H, *p*-C_6H_4OMe), 7.13 (d, 2H, *p*-C_6H_4OMe), 7.47 – 7.80 (m, 15H, PPh_3); $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 2.52 (s, PPh_3); ^{15}N NMR (40.5 MHz, acetone-d_6): δ 200.3 (s, $^{15}N_\alpha$) ; FABMS (NOBA, xenon): m/z 753 (M^+), 725 (M^+ – CO), 618 ($M^+ - N_2C_6H_4OMe$) ; Anal. Calcd: C, 51.49 ; H, 4.45 ; N, 3.34. Found: C, 51.66; H, 4.57 : N, 3.59; Melting Point: 122-126 °C dec.

4.2.9 Preparation of $[(\eta^5\text{-}C_5Me_5)Ir(PPh_3)(CN)(p\text{-}N_2C_6H_4OMe)]$ (7)

After synthesizing $[Cp^*Ir(PPh_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **C** (50 mg; 0.062 mmol) in ethanol (5 mL), excess KCN was added and stirred for 15 min. The orange solution slowly changed to yellowish orange, then slowly formed a yellowish orange precipitate. When no more solid precipitated, the mother liquid was removed and the remaining orange solid was vacuum dried. The isolated solid exhibited low solubility in ethanol, acetone, hexane, and diethyl ether. IR ν(CN) 2108 cm^{-1} (EtOH); ^1H NMR (294K, 100 MHz, acetone-d_6): δ 1.48 (d, J_{P-H} = 2 Hz, 15H, Cp*), 3.75 (s, 3H, *p*-C_6H_4OMe), 6.81 (d, 4H, *p*-C_6H_4OMe), 7.30–7.77 (m, 15H, PPh_3); $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 6.99 (s, PPh_3); ^{15}N NMR (40.5 MHz, acetone-d_6): δ 247.5 (s, $^{15}N_\alpha$) ; EIMS: m/z 723 (M^+ – CN, 2H), 590 ($M^+ - N_2C_6H_4OMe$, CN, 2H)

REFERENCES

1. Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. in *Comprehensive Coordination Chemistry*. Vol. 2. Edited by Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Pergamon Press, Oxford, **1987**, p. 130.
2. Sutton, D., *Chem. Rev.* **1993**, 93, 995.
3. Sutton, D., *Chem. Soc. Rev.* **1975**, 4, 443.
4. Krogsrud, S.; Ibers, J. A. *Inorg. Chem.* **1975**, 14, 2298.
5. Cobbledick, R. E.; Einstein, F. W. B.; Farrell, N.; Gilchrist, A. B.; Sutton, D. *J. Chem. Soc. Dalton Trans.* **1977**, 373.
6. Haymore, B. L. ; Ibers, J. A. *Inorg. Chem.* **1975**, 14, 2784.
7. Douglas, P.G.; Galbraith, A. R.; Shaw, B. L. *Trans. Met. Chem.* **1975**, 1, 17.
8. Mason, R.; Thomas, K. M.; Zubieta, J. A.; Douglas, P.G.; Galbraith, A. R.; Shaw, B. L. *J. Am. Chem. Soc.* **1974**, 96, 260.
9. Bishop, M.W.; Butler, G.; Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc. Dalton Trans.* **1979**, 1843.
10. Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, 97, 5369.
11. Dilworth, J. R.; Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc. Chem. Commun.* **1983**, 1368.
12. Dart, J. W.; Lloyd, M. K.; Mason, R.; McCleverty, J. A. *J. Chem. Soc. Dalton Trans.* **1973**, 2039.
13. Abel, E. W.; Burton, C. A.; Churchill, M. R.; Lin, K. G. *J. Chem. Soc. Chem. Commun.* **1974**, 268.
14. Connelly, N. G.; Demidowicz, Z. *J. Organomet. Chem.* **1974**, 73, C31.
15. Gaughan, A. P.; Haymore, B. L.; Ibers, J. A.; Myers, W. H.; Nappier, T. E.; Meek, D. W. *J. Am. Chem. Soc.* **1973**, 95, 6859.
16. Gaughan, A. P.; Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**,14, 352.

17. Frost, V. L.; Henderson, R. A. *J. Chem. Soc. Dalton Trans.* **1985**, 2059.

18. Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc. Dalton Trans.* **1973**, 2713.

19. Einstein, F. W. B.; Sutton, D. *J. Chem. Soc. Dalton Trans.* **1973**, 434.

20. Haymore, B. L.; Hughes, M.; Mason, J.; Raymond, R. L. *J. Chem. Soc. Dalton Trans.* **1988**, 2935.

21. Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc. Chem. Commun.* **1973**, 176.

22. Baird, M. C.; Wilkinson, G. *J. Chem. Soc. (A).* **1967**, 865.

23. Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, 95, 3052.

24. Parshall, G. W. *J. Am. Chem. Soc.* **1965**, 87, 2133.

25. Parshall, G. W. *J. Am. Chem. Soc.* **1967**, 89, 1822.

26. Yan, X.; Einstein, F. W. B.; Sutton, D. *Can. J. Chem.* Submitted.

27. Tolman, C. A. *Chem. Rev.* **1977**, 77, 314.

28. Cenini, S.; Ugo, R. *J. Chem. Soc. (A).* **1971**, 3441.

29. Duckworth, V. F.; Douglas, P. G.; Mason, R.; Shaw, B. L. *J. Chem. Soc. Chem. Commun.*, **1970**, 1083.

30. Hillhouse, G. L.; Haymore, B. L.; Herrmann, W. A. *Inorg. Chem.* **1979**, 18, 2423.

31. Haymore, B. L.; Ibers, J. A. *Inorg.Chem.* **1975**, 14, 1369.

32. McArdle, J. U.; Schultz, A. J.; Corden, B. J.; Eisenberg, R. *Inorg. Chem.* **1973**, 12, 1676.

33. Dilworth, J. R.; Kan, C. T.; Richards, R. L.; Mason, J.; Stenhouse, I. A. *J. Organomet. Chem.* **1980**, 201, C24.

34. Einstein, F. W. B.; Yan, X.; Sutton, D. *J. Chem. Soc. Chem. Commun.* **1990**, 21, 1466.

35. Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969,** 91, 5970.

36. Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc.* **1970**, 2875.

37. Yan, X. Ph.D. Thesis, Simon Fraser University, **1993.**

38. Brunner, H.; Hammer, B.; Kruger, C.; Angermund, K.; Bernal, I. *Organometallics* **1985**, 4, 1063.

39. Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, 23, 2376.

40. Hunter, G.; Weakley, T. J. R. *J. Chem. Soc. Dalton Trans.* **1987**, 1545.

41. Fujihara, T.; Kaizaki, S. *J. Chem. Soc. Dalton Trans.* **1993**, 1275.

42. Eller, S.; Schwarz, P.; Brimah, A. K.; Fischer, R. D. *Organometallics* **1993**, 12, 3232.

43. Ittel, S. D. ; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, 96, 4804.

44. Mason, J. *Chem Rev.* **1981**, 81, 205.

45. Carroll, J. A.; Fisher, D. R.; Rayner Canham, G. W.; Sutton, D. *Can. J. Chem.* **1974**, 52,1914.

46. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, **1986**, p. 272.

47. Schramm, K. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1978,** 100, 2932.

48. Barrientos-Penna, C. F.; Einstein, F. W. B. ; Sutton, D.; Willis, A. C. *Inorg. Chem.* **1980**, 19, 2740.

49. Cowie, M.; Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, 98, 7608.

50. Barrientos-Penna, C. F.; Sutton, D. *J. Chem. Soc. Chem. Commun.* **1980**, 111.

51. Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, 21, 2578.