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RESEARCH ARTICLE

IRIDIUM (III) –HYDRIDOCYCLOMETALLATED-IMINE COMPLEXES, AS A RESULT OF C-H BOND ACTIVATION IN COORDINATED LIGAND, SPECTROSCOPIC STUDIES

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ABSTRACT

I.R., ^{1}H and ^{31}P NMR spectra of the solution of [IrHCl (X-benzylidene) (Y-pyridine) $(PPh_3)_2$] and [IrHCl(X-benzylidene) (Y-thiazole) (($PPh_3)_2$] in $CDCl_3$ show that the hydride resonances absorb in the range of **δ**(-) 14.60 – (-) 15.04 ppm for pyridines complexes and in the range of **δ** (-) 15.46 – (-) 19.98 ppm for imidazole's complexes. The hydride complexes formation strongly suggest that oxidative addition of CH=N to iridium take place by =C-H bond activation of the imine ligand. The disposition of the hydride ligand was inferred as trans to a N-donor ligand. The ^{31}P-chemical shifts for the phosphorous atom bonded to Ir falls in the range of **δ**13.20 – 16.14 ppm.

INTRODUCTION

The cyclometallated complexes represent one of the most interesting and broadly studied class of organo-transition metal complexes. Although there is a strong interest in studying the mechanism of this bond-activation process, cyclometallation is a highly attractive and versatile synthetic approach for generating organometallic systems, with very important potential (Crabtree, 2005). There are both mononuclear and binuclear species, but also polynuclear cyclometalated complexes are known (Diez *et al*., 2002). May reviews and books have been dedicated to this topic over the past years and one of the most recent can be found here (Albrecht, 2010). Cyclometallation process consists of a transition metal-mediated activation of a C-R bond to form a metallacylcle that contain a metal-carbon sigma-bonded (Hill, 2002). On the other hand, cyclometallation can be regarded as a special case of oxidative addition, in which a C-R (in most cases, C-H) bond in a ligand oxdatively adds to a metal to give rise to a ring compound. Insertion of metals into C-H have been observed with both the quinolines and Schiff base substrate (Dehand and Pfeffer, 1976).

Complexes that undergo this reaction include [RhCl (PPh_3)], [$RhX2Cl_2$], (X=C_2H_4 or CO), [$MCl(\mu\text{-}Cl)PR_3)]_2$, [M=Pd(II) or Pt(II)] and [$MCl(\mu\text{-}Cl)$ $(cyclooctene)_2]_2$, [M= iridium (I) or rhodium (I)] (Albinati *et al*., 1987; Suggs, 1985; Dowerah *et al*., 1990 and Suggs, 1979). However, C-C insertion has been reported only for the quinoline series (Suggs, 1985; Dowerah *et al*., 1990; Suggs, 1979 and Suggs and Chul-Ho, 1985) and is apparently a more demanding reaction, both statically and electronically. Nevertheless the ethylene complex [Rh $(C_2H_4)_2Cl]_2$ has been shown to undergo C-C insertion with a variety of 8-quinolyl-COR ketones (Garber *et al*., 1975). In most recent application for ruthenium, rhodium and iridium complexes have been used as therapeutic agents and a number of kinetically inert ruthenium (II), iridium (III) and rhodium (III) complexes have been reported as inhibitors of protein kinases (Leung *et al*., 2013; Zhong *et al*., 2014; Liu t al., 2014; Ma *et al*., 2014 and Leung *et al*., 2012). Chung-Hang Leung and Dik-Lung Ma group (Liu *et al*., 2014) has also actively pursued the development of kinetically inert metal complexes as inhibitors of various bimolecular targets, including DNA, enzymes and protein–protein interactions (Zhong *et al*., 2014). The synthesis and characterization of a variety of new iridium (III) complexes of [X-(benzylideneamino) pyridines], (Scheme1) and [X-benzylideneamino] thiazoles (Scheme 2), in

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which the imines C-H has undergone oxidative addition to the metal is reported here.

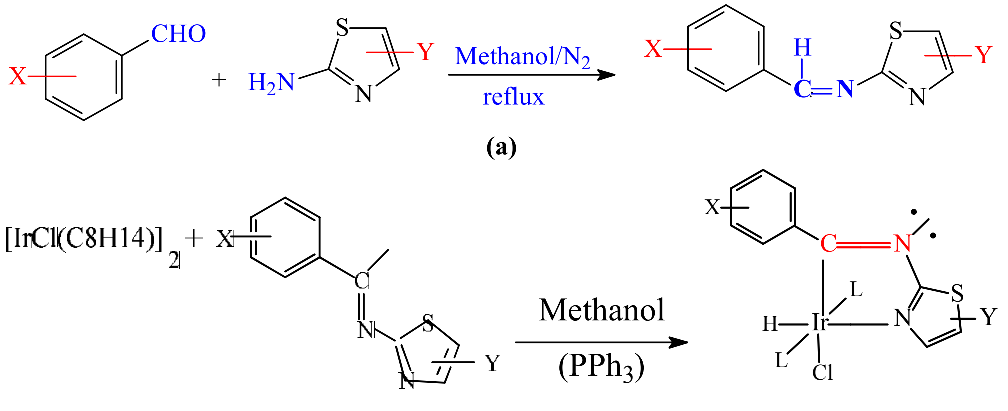
Experimental

Material and Reagents: All chemicals used such as thaizole and pyridine substituents, $IrCl_3xH_2O$, tri phenyl phosphine (PPh_3), cyclooctene, tetrahydrofuran (THF) were obtained from Win lab, Aldrich Chemicals and Strem chemicals, and were used without further purification.

Instruments: Open capillaries were used to determine melting points and were uncorrected using Gallenkamp Melting Points Apparatus. Elemental microanalysis of the separated solid chelates for C, H, N, were performed at Perkin Elmer 2400 CHN. The analyses were repeated twice to check the accuracy of the results obtained. Infrared Spectra were recorded on a Nexus 470-670-760 spectrometer and FT-IR Spectrometer, Spectrum 8400s. The ^1H, and ^{31}P NMR spectra were recorded using 400 MHz Joel Spectrometer.

Synthesis of ligands: All experiments were carried out under an atmosphere of nitrogen. By Schlenk techniques. The Schiff bases were prepared by mixing equivalent amount of substituted benzaldehydes and 2-aminopyridine (or 2-aminothiazole) derivatives in present of methanol. This mixture was boiled under reflux with stirring for 8h, at 80°C in an oil bath, then the mixture was concentrated by rotary evaporation to give yellow precipitate. Filtered off, dried, give 80-90 % yield, Schemes (1 and 2). The data for UV, IR, ^1H and ^{13}C, Spectroscopy and elemental analyses for free Schiff bases published elsewhere (Alsaygh and Humaidan, 2014).

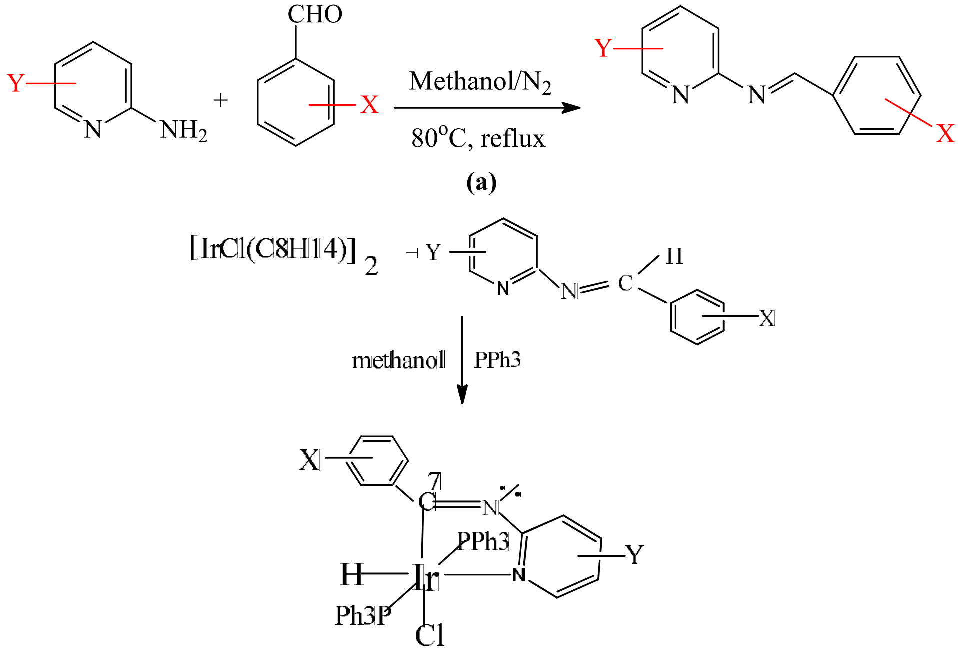
Synthesis of iridium complexes: Synthesis of iridium complex chlorobis (cyclooctene) iridium(I)dimer: $\{IrCl(C_8H_{12})_2\}_2$ were prepared by literature procedures (Angelici *et al.*, 2007). The iridium cyclometallated complexes in this work were prepared by the reaction of the Schiff base with : $\{IrCl(C_8H_{12})_2\}_2$.



(a)

(b)

Scheme 1. Synthesis of a) [X-benzylideneamino]thiazoles] Schiff bases ligands and b) Synthesis of new iridium (III) complex of [X-benzylideneamino] thiazoles



(a)

(b)

Scheme 2. Synthesis of Schiff bases ligands of a) [X-(benzylideneamino) pyridines] ligands and b) Synthesis of new iridium (III) complexes of [X-(benzylideneamino) pyridines]

A typical exemplar are described here:

A solution containing $\{IrCl\ (C_8H_{14})_2\}_2$ (134mg, 0.2mmol) and two equivalents amount of Schiff base (0.4 mmole) and four equivalents of triphenyl phosphine (PPh_3), (211mg, 0.8mmole (orbenzyldiphenyl phosphine) in ca. 20ml, of dry THF was boiled under reflux for 1h under nitrogen atmosphere. After cooling, orange powder which was filtered off (the product be recrystallized from CH_2Cl_2/hexane, Scheme (1and2). The CHN and melting points analyses were carried out and the results were recorded in Table (1). The ^{1}HNMR spectroscopy for hydride complexes, and ^{31}P-NMR spectroscopy were recorded in Table (2).

Table 1. CHN data and melting points analyses for iridium complexes (1-9)

No.	X	L	M.P. (°C)	M.F.	Calculated (%)			Found (%)		
					C	H	N	C	H	N
1.	2-OH	$BzPh_2P$	195	IrC49H44N2SOP2Cl	58.93	4.41	2.81	58.87	4.31	2.83
2.	2-OH	PPh_3	210	IrC45H40N2SOP2Cl	57.11	4.28	2.96	57.36	4.21	2.93
3.	H	$BzPh_2P$	134	$IrC_{49}H_{44}N_2SP_2Cl$	59.91	4.48	2.85	59.84	4.45	2.81
4.	H	PPh_3	266	$IrC_{45}H_{40}N_2SP_2Cl$	58.10	4.30	3.01	58.17	4.28	3.12
5.	2-OH	PPh_3	205	IrC49H42P2N2OCl	61.03	4.36	2.91	61.05	4.44	3.01
6.	4-NO2	PPh_3	152	IrC49H41P2N3O2Cl	59.24	4.13	4.23	59.25	4.17	4.34
7.	2-OH	PPh_3	180	IrC49H42P2N2OCl	57.11	4.28	2.96	57.30	4.24	2.88
8.	4-Br	PPh_3	175	IrC49H41P2N2BrCl	57.28	3.99	2.73	57.34	4.01	2.77
9.	4-Br	PPh_3	205	IrC48H38P2N2BrCl2	55.01	3.63	2.67	55.23	3.66	2.68

Y: No.1, 2, 3, 4,7 and8 =4-CH3. No. 5, 6= 3-CH3 and No. 9 = 5- Cl.

Table 2. The ^{1}H, ^{31}P NMR and ^{2}J (^{31}P-^{1}H) spectra of some iridium complexes

Compound No	X	Y	L	δ (Ir-H) ppm	δ ^{31}P{^{1}H}	^{2}J(^{31}P-^{1}H) (Hz)
1.	2-OH	4-Me	$BzPh_2P$	-19.98	n	13.94
2.	2-OH	4-Me	PPh_3	-15.97	4.38	15.70
3.	H	4-Me	$BzPh_2P$	-19.78	n	13.20
4.	H	4-Me	PPh_3	-15.46	3.83	15.88
5.	2-OH	3-Me	PPh_3	-14.91	2.43	15.80
6.	4-NO2	3-Me	PPh_3	-14.60	2.70	16.00
7.	2-OH	4-Me	PPh_3	-15.04	n	16.14
8.	4-Br	4-Me	PPh_3	-15.00	n	16.10
9.	4-Br	5-Cl	PPh_3	-14.75	n	13.22

n=not determined

RESULTS AND DISCUSSION

Schiff bases (1-4), have been obtained by the reaction of 2-aminothiazoles with aromatic aldehydes (Scheme 1-a), and Schiff bases (5-9) have been obtained with the reaction of 2-aminopyridines and aromatic aldehydes (Scheme 2-a). The iridium (III) cyclometallated complexes were prepared by refluxing two equivalents of Schiff base and four equivalent PR3, with $[IrCl\ (C_8H_{14})_2]_2$ in THF for 1h, (PR3=PPh3, PPh2CH2Ph) as depicted in Schemes (1-b and 2-b).

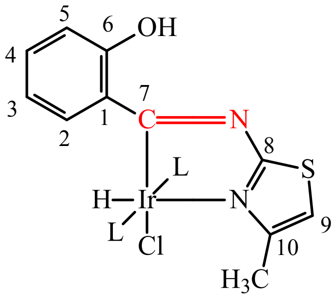
Characterization of Iridium-Complexes

Infrared Spectra

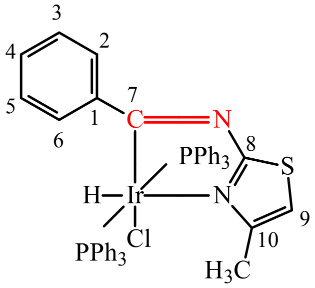
Infrared spectra of the complexes were recorded to confirm complex structure. The vibration frequencies and their tentative assignments for Schiff bases ligand (Scheme 1, 2) and their iridium -complexes were assigned by comparison with the vibrational frequencies of the free ligand and their related complexes. The main futures in the infrared of the complexes is the absent of the shift of the stretching frequencies of the azomethine (ν -C=N-) group for free imines of complexes (1-4) in the range, ν 1570-1620cm^{-1}, and in the range, ν 1590-1620, for free imines of complexes (5-9) due to the coordination of the azomethine moiety, to the iridium metal (Nakamoto, 1997). Evidence of the bonding obtained from the observation of new bands in the spectra of the metal complexes at ν (i.e.2181.49 cm-1 for complex No.1) as a result of formation of Ir-H bond, this results in agreement with many Ir-H bond in the literature (Usatov *et al.*, 1996). and the observation of new bandsof medium or weak intensity at the region 467-435 cm^{-1} due to ν(M-N) stretching vibration supporting the involvement of the nitrogen atom of the azomethine group via coordination (Hanif and Chohan, 2013 and Abou-Hussain and Linert, 2014), (Figure 1), complex (1). This is in agreement with published results for ν Ir-H in similar complexes (Usatov *et al.*, 1996 and Abou-Hussain and Linert, 2014). A strong evidence come from the spectra of ^{1}H and ^{31}P NMR (Table 2).

^{1}H and ^{31}P NMR Spectra

The ^{1}H and ^{31}P NMR spectra of the iridium complexes have been studied in $CDCl_3$. The ^{1}H NMR spectrum of each of the new iridium complexes in $CDCl_3$, shows a hydride resonance between **δ**(-) 14.60 – (-) 15.04 ppm for pyridines complexes and in the range of **δ** (-) 15.46 – (-) 19.98 ppm for imidazole's complexes (Table 2). The imines C-H signals for the starting free imines appear at δ 9.01-9.44ppm and after complexation these signals are absent, providing evidence for insertion of Ir metal into the C-H bond of the imines. Strong confirmation evidence comes from appearance of the resonance of the hydride signal in each complex at high field (Foot and Heaton, 1973 and Wentzel, 2011), ca. (average) δ -17.29 ppm. The hydride signals in the complexes are split by coupling to two un-equivalents ^{31}P nuclei. As both of these spin-spin couplings are ca. 13.20-16.14Hz, frequently, ^{2J} (^{31}P-^{1}H), (Table 2). The hydride doublet of doublet often appears as a triplet due to the coupling between ^{31}P and ^{1}H, ^{2}J (^{31}P-^{1}H) ca. 13.20-16.14Hz, (Figure 2 and 3), complexes (2 and 4). The phosphine (PPh_3) iridium complexes (Figure 4 and 5), complexes (2 and 4),



L= Ph$_2$BzP



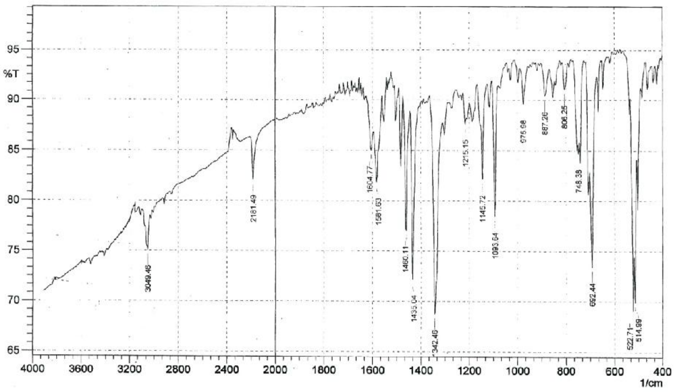


Figure 1. I.R. Spectra for complex (1)

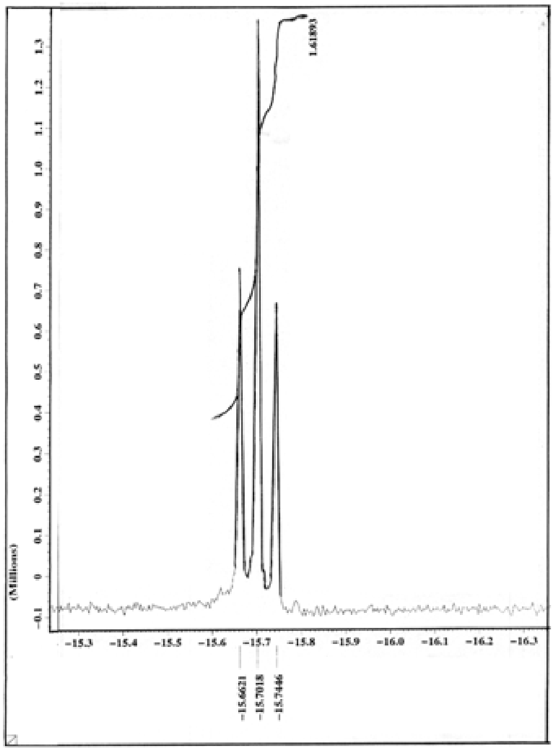


Figure 3. ^{1}H-NMR spectra for complex (4)

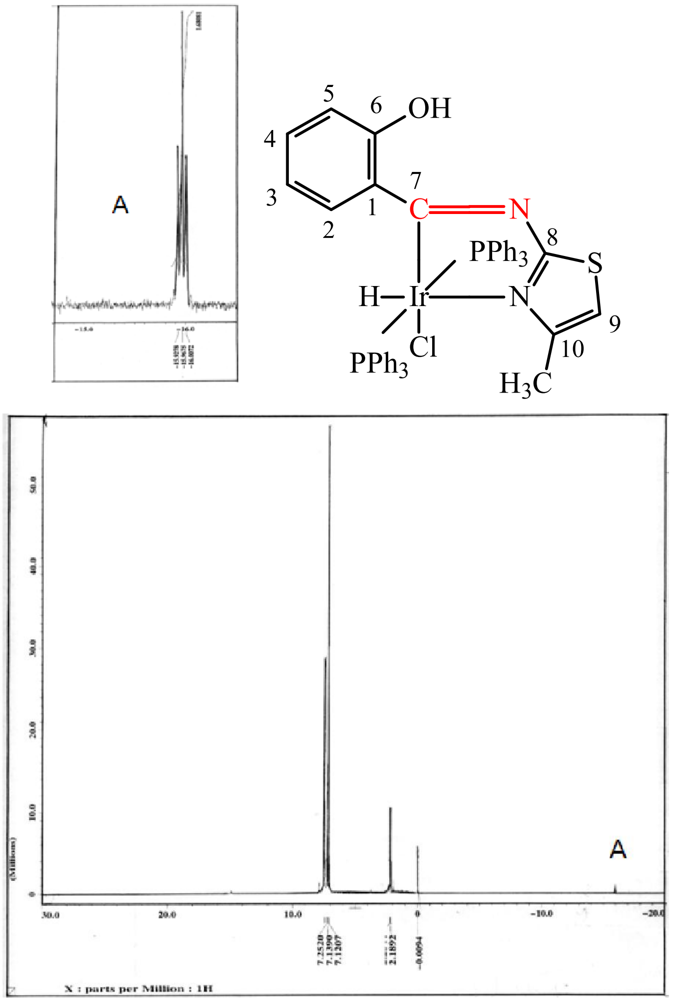


Figure 2. ^{1}H-NMR spectra for complex (2)

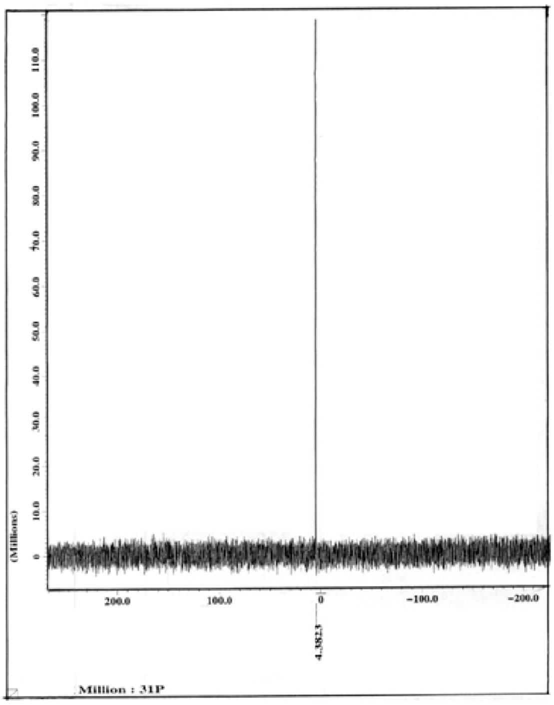


Figure 4. ^{31}P-NMR spectra for complex (2)

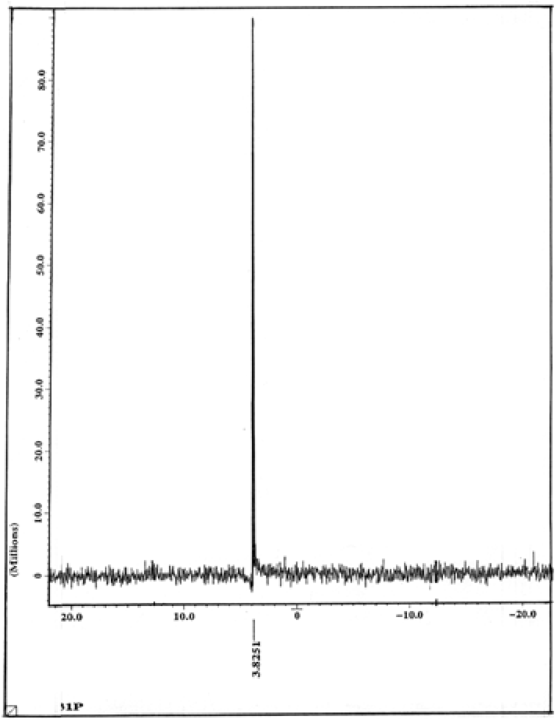


Figure 5. ^{31}P-NMR spectra for complex (4)

show a ^{31}P signal at δ4.38and δ 3.83 ppm respectively, this may be due to the 2J (P-H) constant is too low to be observed and due to low solubility in CDCl3 (Table 6). Keeping with previous report (Suggs and Chul-Ho, 1984), depending on the type of the substituent group on thiazole or pyridine ring (Table 2). The majority of the iridium imine hydride complexes are only moderately soluble in most organic solvents and no 13C-NMR detected. The remaining 1H and 31P-NMR data are as expected. Steric effects are extremely important to structures, spectroscopic properties, and chemical behavior of phosphorus ligands and their complexes (Hanif and Chohan, 2013). In this study two types of phosphorus ligands (PPh_3 and $PBzPh_2$) were used with different steric and electronic effects. The cone-angle data of Tolman (Albinati *et al.*, 1987 and Tolman, 1977) allows some comparisons of relative ligand steric effects to be made and demonstrates phosphine ligands such as $PBzPh_2$ (ca. 153o) and PPh_3 (ca. 145o). Increasing the size of the substituents on phosphorus will tend to reduce the s characters in the phosphorus long pair, thus decreasing ^2J (^1H-^{31}P) (Tolman, 1977).

Data from Table (5), shows the δ (^1H-Ir) at -19.98ppm, with ^2J (^{31}P-^1H) 13.94ppm, when ligand BzPh2P (complex No. 1) and δ (^1H-Ir) at -15.97ppm with ^2J (^{31}P-^1H) 15.70Hz, (complex No. 2) when ligand PPh_3 (Tolman, 1977 and Al-Najjar and Al-Hassan, 1987). The position of the ligand signals in both Ir (v Rh-H, 2181.9cm^{-1}) (Usatov *et al.*, 1996 and Hanif and Chohan, 2013) for complex (1) (Figure 1) and ^1H-NMR (δ-11.29ppm) Spectra, areas expected for anIr-H bond trans to N-donar ligand. Furthermore, the ^2J (^{31}P-^1H) value is consistent with a hydride located cis to two magnetically un-equivalent PPh_3groups) or $BzPh_2P$ (Kaesz and Saillant, 1972), which in turn are mutually trans, as inferred from ^{31}P [^1H] NMR spectrum (Table 2). Interestingly, the hydride and ^{31}P NMR spectrum of complexes 2 and 5, the ^{31}P-NMR which δ-observed at 4.38 and 2.43 ppm respectively and with ^2J (^{31}P-^1H) 15.7Hz and 15.80 Hz respectively (Table 2). This different in δ-chemical shift is due to the presence of thiazole ligand in the Ir-complex (complex No. 2) compared with pyridine ligand as in (complex No. 5). A significant chemical shift signal of ^{31}P was recorded in figures (4) and (5), and datain Table (2). The iridium complexes are only moderately soluble in CDCl3 and CD2Cl2, but soluble in DMSO solvent and the complexes decomposed due to the formation of Ir-DMSO complexes, and the ^{13}C spectra not observed for the reported complexes (in CDCl3). Unfortunately, treatment of some of imines prepared in this work with 1, 5-hexadiene in toluene at 110°C for 6h under [Arc $(PPh_3)_3$] in screw-capped vial, gives only imonoacycloiridium (III) complex. The chromatographic results from the study indicated that the bond between iridium and hydrogen is not active enough, very stable and can't go for further reactions.

Conclusion

The new cyclometallated iridium complexes have been characterized by elemental analysis, IR, ^1H and ^{31}P - NMR spectroscopy. Interestingly the hydride ligand signal in IR (i.e., v 2181.49 cm-1 and ^1H-NMR (i.e., δ-15.97ppm) for complex 2. The result obtained from the spectra were expected for Ir-H group trans position to the N-donar ligand. However, the ^{31}P-NMR for some cyclometallated complexes shows signal at δ 4.38 ppm, for complex (2). Furthermore, the ^2J (^{31}P-^1H) value of 13.20-16.14 Hz account for H cis to two PPh_3-groups, which in turn are mutually trans, as inferred from $^{31}P(^1H)$ NMR spectrum. This result supported from ^1H -NMR spectra. The result from the study indicated that the bond between iridium and hydrogen is not active enough, very stable and can't go for further reactions.

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