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Novel Hydrido-Rhodium (III) Complexes with Some Schiff Bases Derived from Substituted Pyridines and Aryl Amines

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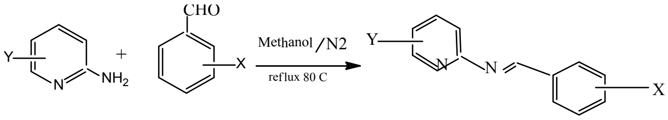
Abstract

A Series of rhodium (III) cyclometallated complexes of the type (RhHCl(NC$_5$H$_2$C=N Ar (PPh$_3$)$_2$} (Ar=Substituted aryl), have been synthesized and characterized. Schiff bases derived from a substituted benzaldehyde and 2-amino pyridine substituents were allowed to react with [RhCl(PPh$_3$)$_3$] or [Rh(μ-Cl)(COD)]$_2$ in the presence of 4 equivalents of PPh$_3$ (or Ph$_2$BzP) to give Rh(III) Cyclometallated complexes, in which the imine C-H bond was added oxidatively to the rhodium metal to give (H-M-C). The complexes were characterized using IR and NMR spectroscopy confirmed by elemental micro-analysis. The absorption of the hydride ligand was inferred as trans to N-donar ligand.

Keywords: Rhodium; Schiff-bases; Phosphine complexes; Hydrido complexes; Oxidative-addition; Ligand substitution

Introduction

Although the Cyclometallation of aromatic and to a lesser extent aliphatic C-H groups is widely recognized [1,2], these are relatively little known concerning with the cyclometallation of aldehydes [3] and imine functions [4-6]. We have shown that Schiff bases of 2-substituted benzylideneaminothiazoles [5], and 2-(benzylideneamino) pyridines [6], can be form cyclometallated complexes at the imine carbon by using Rh (I) complex. A number of studies have exploited ligands such as quindine-8-carbaldehyde [3,7] and 2-(benzylideneamino) pyridines [8]. Complexation of the metal with aromatic nitrogen gives a favorable geometry for the insertion of the metal into the neighboring C-H or C-C bond [4,7,9,10]. 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 [11-15]. Chung-Hang Leung and Dik-Lung Ma group [14] has also actively pursued the development of kinetically inert metal complexes as inhibitors of various bimolecular targets, including DNA, enzymes and protein–protein interactions [13]. The synthesis and characterization of a variety of new rhodium (III) complexes of {N-benzylideneamino} pyridines, in which the imine C-H bond has undergone oxidative addition to the metal, are reported here.



Scheme 1: Syntheses of Schiff's bases ligands.

Complex No.	Y(pyridine)	X(aryl)	Complex No.	Y(pyridine)	X(aryl)
1.	2-OH	H	8.	4-NO$_2$	4-Me
2.	H	3-Me	9.	4-Br	4-Me
3.	2-OH	3-Me	10.	H	5-Cl
4.	4-NO$_2$	3-Me	11.	2-OH	5-Cl
5.	4-Br	3-Me	12.	4-NO$_2$	5-Cl
6.	H	4-Me	13.	4-Br	5-Cl
7.	2-OH	4-Me			

Table 1: The prepared Schiff bases (free ligands).

Experimental

Materials and reagents

All chemicals used such as pyridine substituent's, benzaldehyde substituent's, RhCl$_3$xH$_2$O, phenyl phosphine (PPh$_3$) cyclo-1,5-octadiene (COD), tetrahydrofuran (THF), were obtained from Winlab, Aldrich Chemicals and Strem chemicals, respectively 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 ^{1}H, ^{13}CNMR 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-amino pyridine derivatives in methanol solution. This mixture was boiled under reflux with stirring for 8h, at 80°C in an oil bath, and then the mixture was concentrated by rotary evaporation to give yellow precipitate. Which was filtered off, dried, yields are 70%-80% (Scheme 1,Table 1). The results of UV, IR, ^{1}H and ^{13}C, Spectroscopy and elemental analyses for Schiff's bases were published elsewhere [16].

Rhodium compounds of {RhCl(COD)}$_2$ and {RhCl(PPh$_3$)$_3$} were prepared by literature procedures [17,18]. In this work rhodium cyclometallated complexes, were prepared by the reaction of the Schiff

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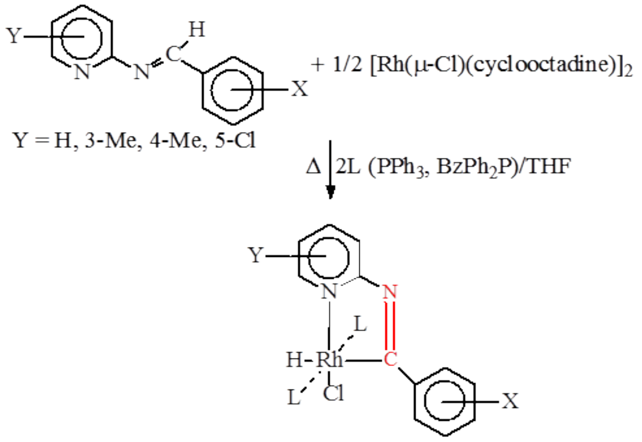
Complex No.	X	Y	L	Complex No.	X	Y	L
14.	2-OH	H	$BzPh_2P$	21.	2-OH	4-Me	PPh_3
15.	2-OH	H	PPh_3	22.	$4-NO_2$	4-Me	PPh_3
16.	H	3-Me	PPh_3	23.	4-Br	4-Me	PPh_3
17.	2-OH	3-Me	PPh_3	24.	H	5-Cl	PPh_3
18.	$4-NO_2$	3-Me	PPh_3	25.	2-OH	5-Cl	PPh_3
19.	4-Br	3-Me	PPh_3	26.	$4-NO_2$	5-Cl	PPh_3
20.	H	4-Me	PPh_3	27.	4-Br	5-Cl	PPh_3

Table 2: The prepared rhodium complexes (14-27).



Scheme 2: Synthesis of rhodium complexes.

No.	L	X	M.P. (°C)	M.F.	Calculated (%)			Found (%)		
					C	H	N	C	H	N
14.	Ph_2BzP	2-OH	137	$RhC_{50}H_{44}P_2N_2OCl$	67.53	5.34	3.15	67.66	5.23	3.34
15.	PPh_3	2-OH	225	$RhC_{48}H_40P_2N_2OCl$	66.94	4.68	3.25	67.30	4.89	3.21
16.	PPh_3	H	84	$RhC_{49}H_{42}P_2N_2Cl$	68.49	4.92	3.26	68.28	4.71	3.47
17.	PPh_3	2-OH	100	$RhC_{49}H_{42}P_2N_2OCl$	67.24	4.83	3.20	67.63	4.82	3.09
18.	PPh_3	$4-NO_2$	140	$RhC_{49}H_{41}P_2N_3O2Cl$	73.46	5.15	5.24	73.35	4.98	5.34
19.	PPh_3	4-Br	98	$RhC_{49}H_{41}P_2N_2BrCl$	70.46	4.94	3.35	69.93	4.93	3.45
20.	PPh_3	H	98	$RhC_{49}H_{42}P_2N_2Cl$	68.49	4.92	3.26	68.28	4.81	3.14
21.	PPh_3	2-OH	139	$RhC_{49}H_{42}P_2N_2OCl$	67.24	4.83	3.2	66.93	4.86	3.34
22.	PPh_3	$4-NO_2$	155	$RhC_{49}H_{41}P_2N_3O2Cl$	73.44	5.15	5.24	73.35	5.01	5.35
23.	PPh_3	4-Br	97	$RhC_{49}H_{41}P_2N_2BrCl$	70.46	4.94	3.35	70.33	4.53	3.13
24.	PPh_3	H	216	$RhC_{48}H_{39}P_2N_2Cl2$	64.40	4.46	3.18	64.53	4.43	3.28
25.	PPh_3	2-OH	349	$RhC_{48}H_{39}P_2N_2OCl2$	64.37	4.38	3.12	64.77	4.48	3.99
26.	PPh_3	$4-NO_2$	192	$RhC_{48}H_{38}P_2N_3O2Cl2$	62.35	4.14	4.54	62.34	4.38	4.58
27.	PPh_3	4-Br	195	$RhC_{48}H_{38}P_2N_2BrCl_2$	60.14	3.99	2.92	60.07	3.96	2.85

Table 3: Physicochemical Properties of the rhodium complexes (14-27).

base with either $\{RhCl(PPh_3)\}$ or with $\{Rh(\mu\text{-}C1)(COD)\}_2$. Two typical examples are described here.

1. A solution containing $\{RhCl(PPh_3)_3\}$ (300 mg, 0.325 mmol) and an equivalent amount of Schiff base (in ca. 20 ml, of dry THF was boiled under reflux for 1 hr under nitrogen atmosphere. After cooling, addition of n-hexane led to precipitation of the product as a yellow powder which was filtered off (the product recrystallized twice from CH_2Cl_2/hexane, yield 40%-50% (Table 2 and Scheme 2).

2. A solution of $\{Rh\ (\mu\text{-}C1)(COD)\}_2$ (200 mg, 0.28 mmol) Schiff base (0.56 mmol) and PPh_3 (293 mg, 1.12 mmol) in ca. 20 ml of dry THF was boiled under reflux for 1 hr addition of n-hexane induced precipitation of the product, which was filtered off (the product could be recrystallized form CH_2Cl_2/hexane (Table 2, Scheme 2).

Results and Discussion

The physical, analytical data and UV, IR, ^1H, ^{13}C-NMR Spectroscopy for Schiff bases were published elsewhere [16]. The corresponding Rh-complexes of different Schiff base ligand are investigated also by analytical, physical and different spectroscopy methods (Tables 3-5).

Characterization of Rh-Complexes

Infrared Spectra: Infrared spectra of the complexes were recorded to confirm their structure. The vibration frequencies and their tentative assignments for imines ligand (Scheme 1) and their Rh-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 shift of the stretching frequencies of the azomethine (-C=N-) group of the transition metal complexes to lower frequencies

Complex No.	X	Y	L	δ ^{1}H Hydride (ppm)	δ ^{31}P{^{1}H} (ppm)	^{2}J(^{31}P-^{1}H) (Hz)	^{1}J(^{103}Rh-^{1}H) (Hz)	^{1}J(^{103}Rh-^{31}P) (Hz)
14.	2-OH	H	$BzPh_2P$	-11.78	25.6	11.00	14.3	105.0
15.	2-OH	H	PPh_3	-11.43	30.2	11.00	13.2	112.0
16.	H	3-Me	PPh_3	-11.20	30.30	12.40	12.3	111
17.	2-OH	3-Me	PPh_3	-11.35	3069	12.42	12.4	112.5
18.	4-NO_2	3-Me	PPh_3	-11.21	30.63	12.45	13.7	114.5
19.	4-Br	3-Me	PPh_3	-11.27	30.65	12.44	13.3	114.3
20.	H	4-Me	PPh_3	-11.19	33.36	11.60	13.44	114.6
21.	2-OH	4-Me	PPh_3	-11.78	33.7	11.00	13.90	112.0
22.	4-OH_2	4-Me	PPh_3	-11.29	31.86	12..24	13.44	114.6
23.	4-Br	4-Me	PPh_3	-11.32	32.69	11.00	12.20	118.0
24.	H	5-Cl	PPh_3	11.19 -11.19	34.67 18.79	11.20	13.41	121.5 98.7
25.	2-OH	5-Cl	PPh_3	-11.41	n	11.23	14.10	n
26.	4-NO_2	5-Cl	PPh_3	-11.31	n	11.0	14.42	n
27.	4-Br	5-Cl	PPh_3	-11.32	20.10 26.82	11.30	14.52	114.3 104.3

n=not measured

Table 4: ^{1}H and ^{31}P NMR (δ ppm) and coupling constants (Hz) of the rhodium complexes (14-27).

Complex No.	X	Y	δ C(7) (ppm)
17.	2-OH	3-Me	235.56
18.	2-NO_2	3-Me	225.16
19.	4-Br	3-Me	236.24
20.	H	4-Me	237.60

Table 5: ^{13}C-NMR for iminoyl carbon (C-7) (δ ppm) in the rhodium complexes (17-20).

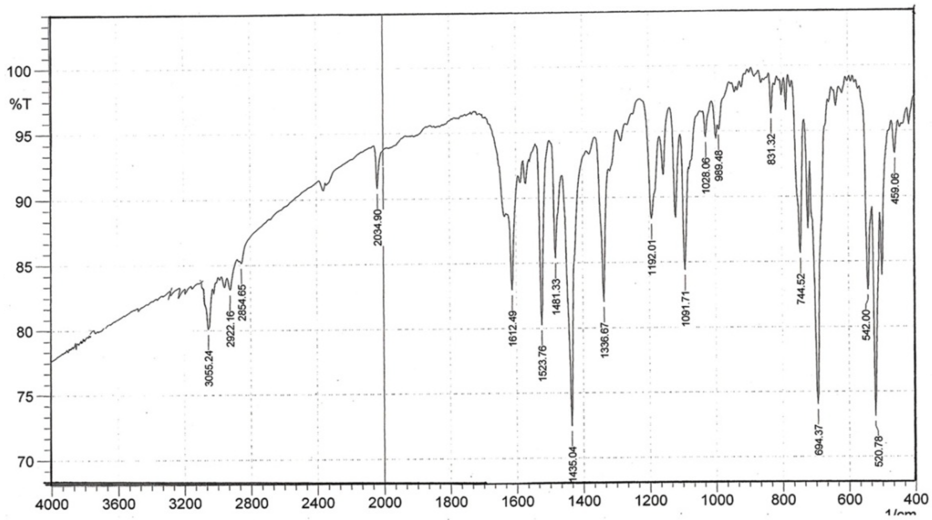


Figure 1: IR Spectra for complex (22).

in the range, 1600-1576 cm^{-1}, compared with free imine ligand, v(1690-1620 cm^{-1}) due to the coordination of the azomethine moiety, v(C=N) to the metal [19]. Further evidence of the bonding is given by the observation of new bands in the spectra of the metal complexes of medium or week intensity at the region 467-435 cm^{-1} due to v(M-N) stretching vibration supporting the involvement of the nitrogen atom of the azomethine group via coordination [20,21] (Figure 1), complex (22). Further evidence come from the spectra of ^{1}H, ^{13}C and ^{31}P NMR (Tables 4 and 5).

^{1}H, ^{13}C and ^{31}P NMR Spectra: The ^{1}H, ^{13}C and ^{31}P NMR spectra of the rhodium complexes have been studied in $CDCl_3$. The ^{1}H NMR spectrum of each of the new rhodium complexes in $CDCl_3$, shows a hydride resonance between δ11.19-11.78 ppm (Table 4). The imines C-H signals for the starting free imines appear at δ 9.01-9.44 ppm and after complexation these signals are absent, providing evidence for insertion of Rh 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 [22,23], ca. (average) δ -11.29 ppm. The hydride signals in the complexes are split by compiling to two equivalent ^{31}P nuclei of the rhodium complex. As both of these spin-spin couplings are ca. 11.00-14.52Hz, frequently. ^{1}J (^{103}Rh-^{1}H). Hz, and 2J (^{31}P-^{1}H), ca. 11.00 - 12.45 Hz (Table 4). The hydride multiple often appears as a pseudo quartet, but at higher resolution studies usually reveal the expected doublet of triplets (Figure 2 and Figure 3), complexes (23 and 24) .The phosphine (PPh_3) rhodium complexes

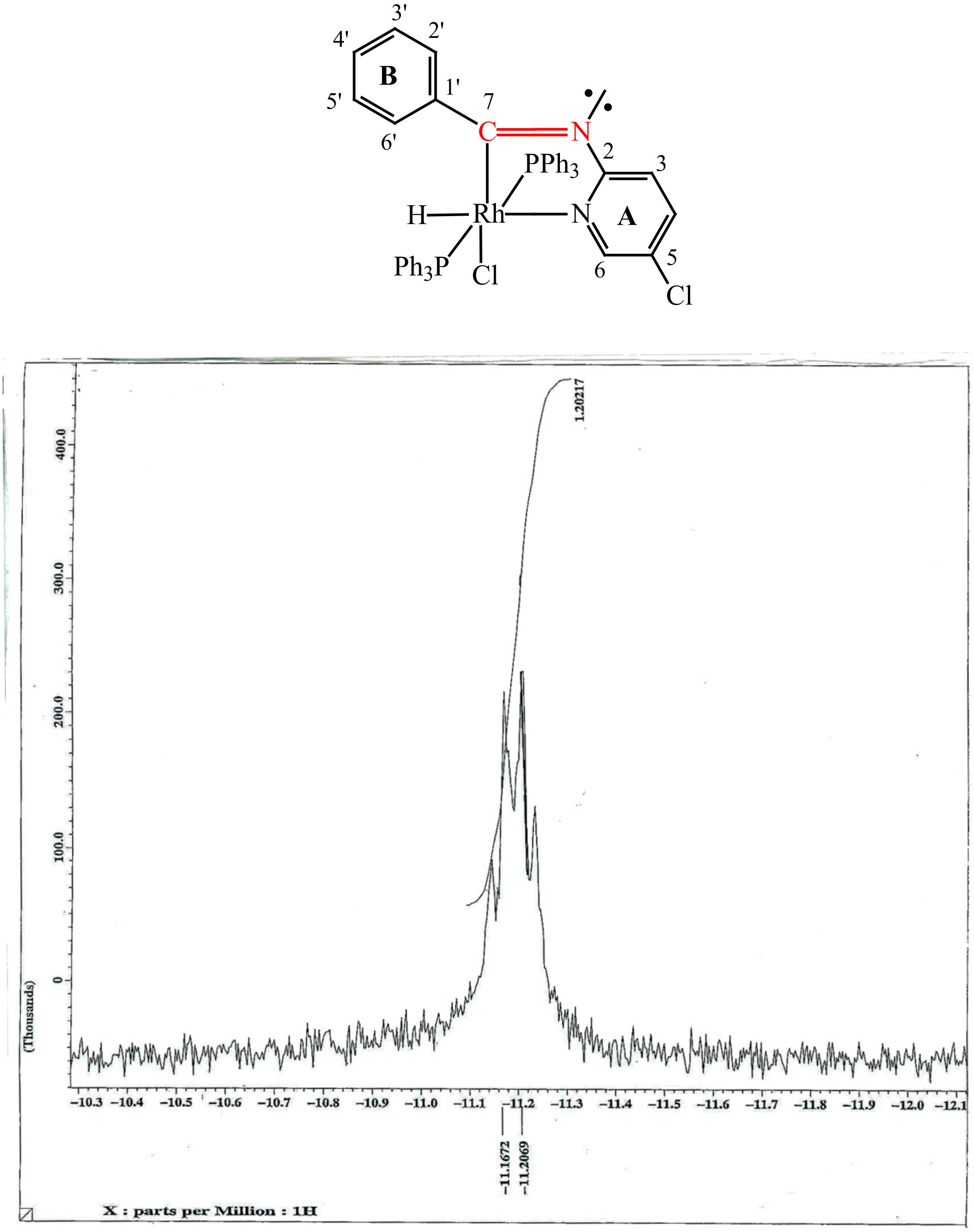


Figure 2: ^{1}H NMR (hydride) spectra for complex (23).

(Figure 4 and Figure 5), complexes (24 and 27), show a ^{31}P signal at ca. 18.79-34.67 Hz, (Table 4), with $^{1}J(^{103}Rh-^{31}P)$ 98.7-118.0 Hz as a doublet in keeping with previous report [3,10,16], depending on the type of the substituent group on pyridine ring (Table 4). The majority of the rhodium imine hydride complexes are only moderately soluble in most organic solvents. The signal of $^{13}C{=}N$ of the imino group is observed at ca. δ 225.06-237.60ppm (Table 5). The ^{13}C [^{1}H] NMR spectrum, in particular the signal from the metal-bonded carbon atom, is consistent with the presence of the cyclometallated ring [22,23]. The signal from the metal-bonded carbon, C(7) (iminoyl carbon), appear as a doublet or triplets owing to coupling of two equivalent ^{31}P nuclei and the ^{103}Rh nucleus, whereas the corresponding signal from the uncomplexed imines is found at ca. δ146.24-164.97 ppm [22]. This low-field position for C(7) has been observed in other cases in what a chelating atom is incorporated in a five member-ring [24], and is not unusual for a cyclometallated sp^2 carbon [25], similar to carbene-carbon. The remaining ^{1}H and ^{13}C data are as expected. Steric effects are extremely important to structures, spectroscopic properties, and

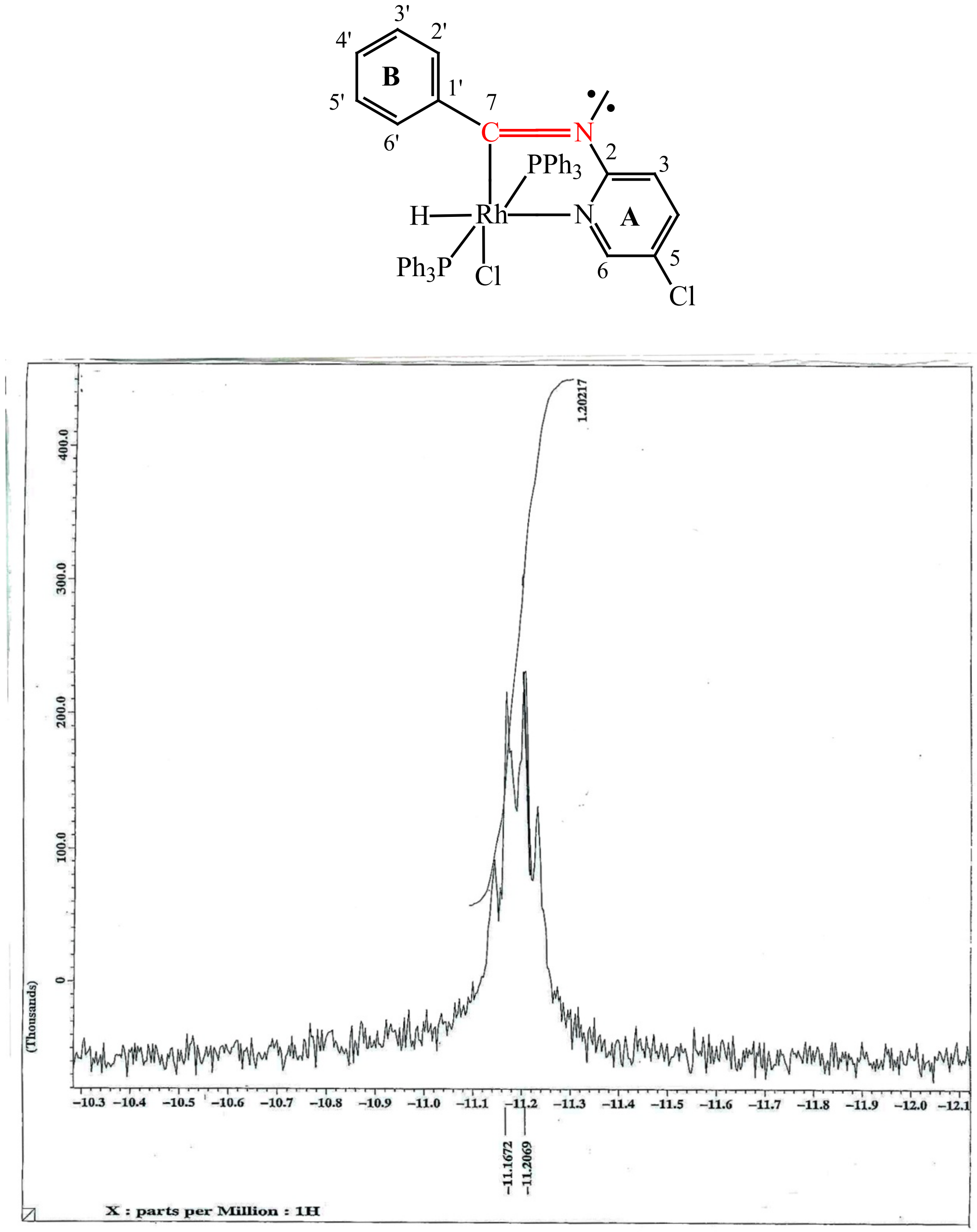


Figure 3: ^{1}H NMR (hydride) spectra for complex [24].

chemical behavior of phosphorus ligands and their complexes [26]. 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 [27] allows some comparisons of relative ligand steric effects to be made and demonstrates phosphine ligands such as $PBzPh_2$ (ca. 153°) and PPh_3(ca. 145°). Increasing the size of the substituents on phosphorus will tend to reduce the s character in the phosphorus long pair, thus decreasing ^1J(M-P)[21]. Data from Table 5, shows the $\delta\,^{31}P$ [^1H] at 25.60ppm, with ^1J (^{103}Rh-^{31}P), 112.0Hz when ligand BzPh2P and $\delta\,^{31}P$ [^1H] at 105.0Hz with ^1J (^{103}Rh-^{31}P), 105.0Hz when ligand PPh_3 [27,28].

The position of the ligand signals in both IR(v Rh-H, 2034.9cm^{-1}) for complex 22 (Figure 1) and ^{1}H-NMR (δ-11.29ppm) Spectra, are as expected for a Rh-H bond trans to N-donor ligand. Furthermore,

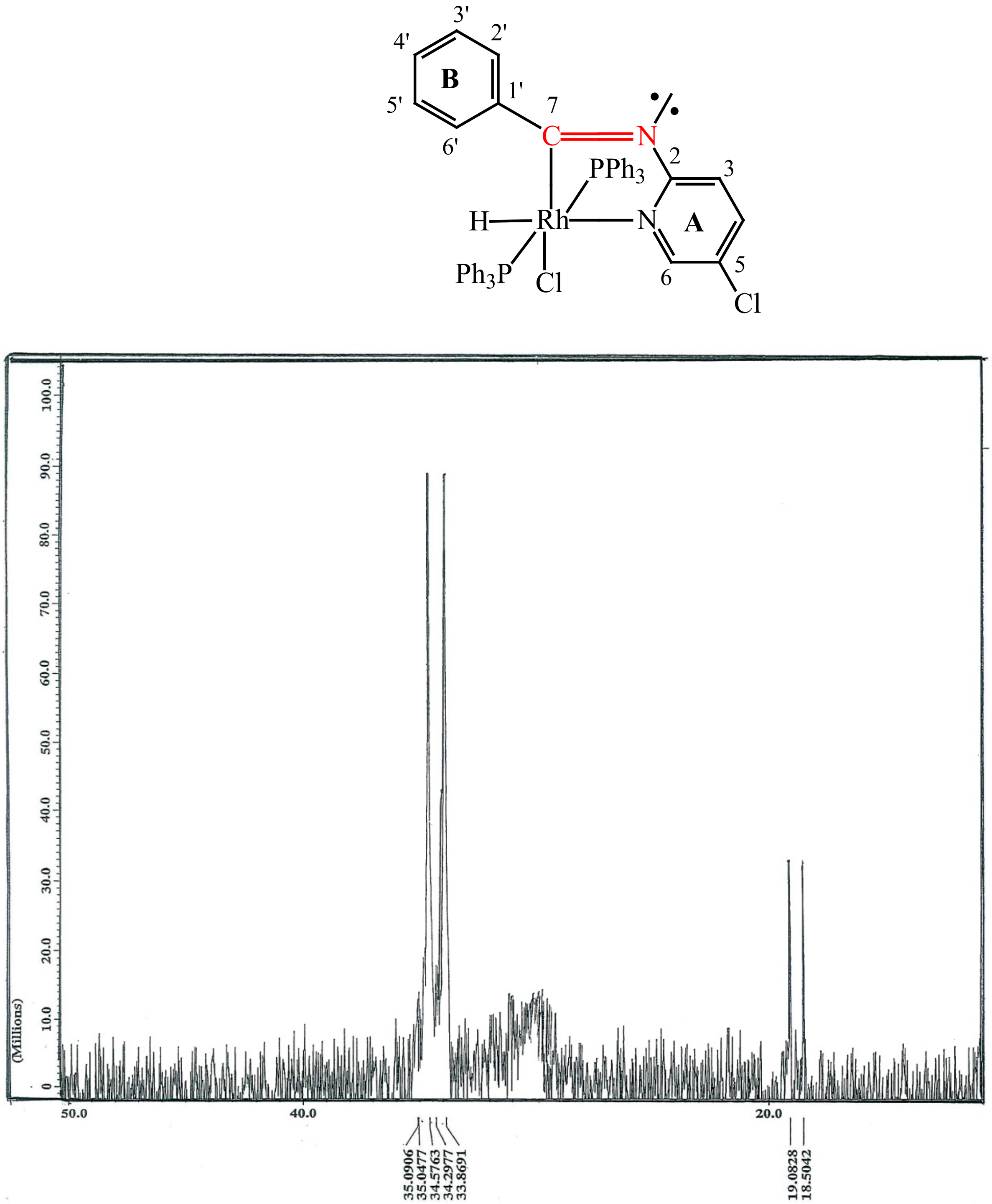


Figure 4: ^{31}P NMR spectra for complex (24).

the $^{1}J(^{31}P\text{-}1H)$ value is consistent with a hydride located cis to two magnetically equivalent PPh_3 groups [29], which in turn are mutually trans, as inferred from ^{31}P [^{1}H]NMR spectrum (Table 4).

Interestingly, the hydride and ^{31}P NMR spectrum of complexes 24 and 27, the ^{31}P-NMR presented in two types of spectrum, for ^{31}P-NMR-spectra , which δ -observed at 34.67 and 18.79 ppm (for complex 24), and at δ 20.10 and 26.82 ppm (for complex 27), with ^{2}J ($^{31}P\text{-}^{1}H$) 11.20Hz and 11.30 Hz , (Figure 4 and Figure 5) respectively, and with $^{1}J(^{103}Rh\text{-}^{31}P)$, of 121.50 Hz , 98.70 Hz and 121.50, 104.2 Hz respectively (Table 4).

This result may be due to complex instability. The similarity of present of Cl- atom at C5 results of two or three ^{31}P absorption spectrum. By substitution of Br-atom at C-4 of aryl ring (Figure 5) a significant change in signal of ^{31}P was recorded in Figures 4,5 and Table 4. It was also observed that the signal for C-7 (iminoyl carbon $^{13}C=N$) is

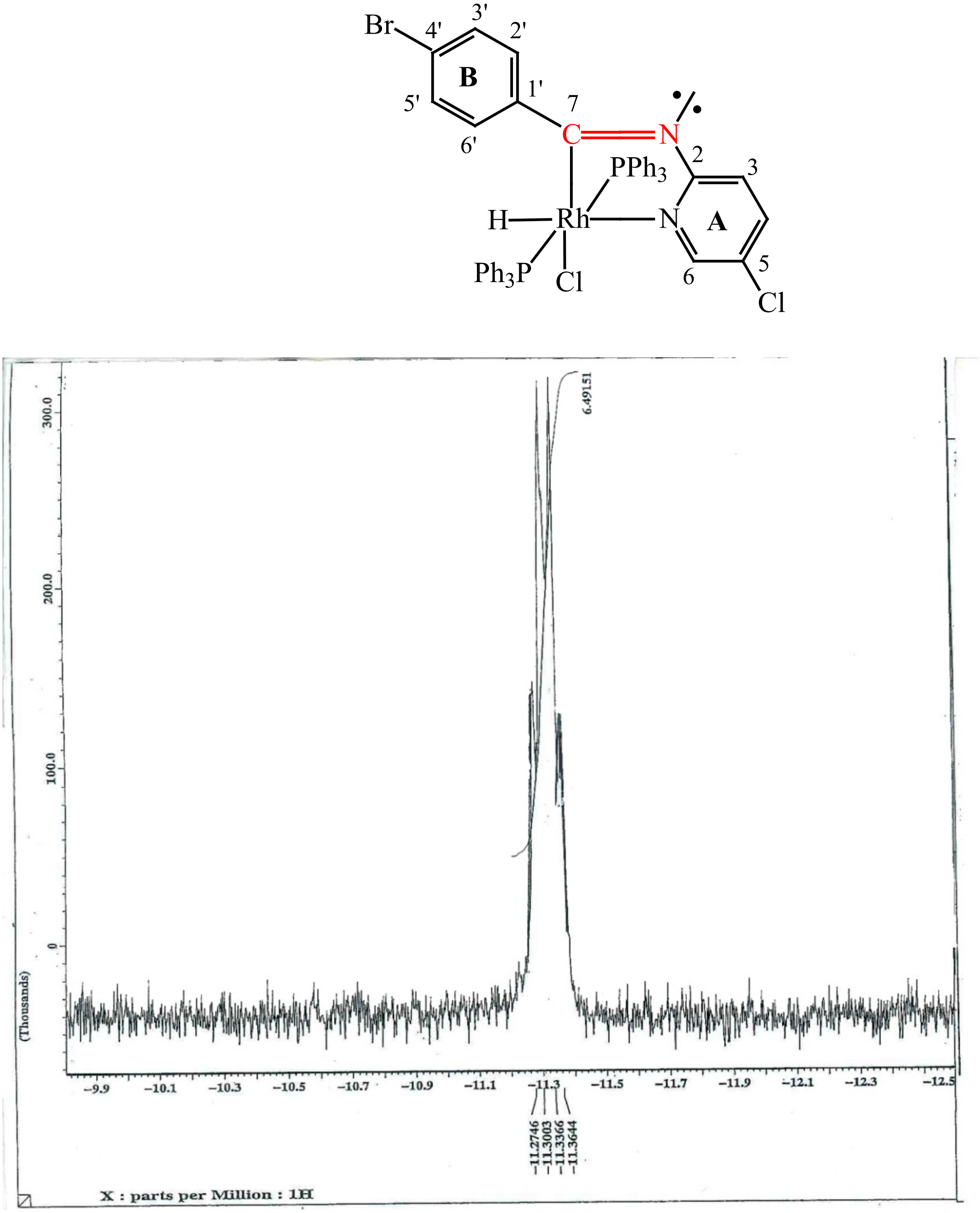


Figure 5: ^{1}H NMR spectra for complex (27).

at low magnetic field, at δ225.16-237.60ppm with ^1J (^{103}Rh-^{13}C), 32-33 Hz and ^2J (^{31}P-^{13}C), 8-9Hz (Table 5).

The rhodium complexes are only moderately soluble in organic solvents, and so we have not obtained many ^{13}C spectra, however, some ^{13}C (7) data for few complexes are shown in Table 5. The signal for C-7 is all at 225.16-237.60 ppm, whereas the uncomplexed imines C-7 signal is found at δ159.39-164.97 ppm. This low field position is suggestive of carbine-like properties; however, the δ ^{13}C=N for complex (24) is observed at low magnetic field at δ 237.67ppm (Table 5 and Figure 6).

Unfortunately, treatment of some of imines prepared in this work

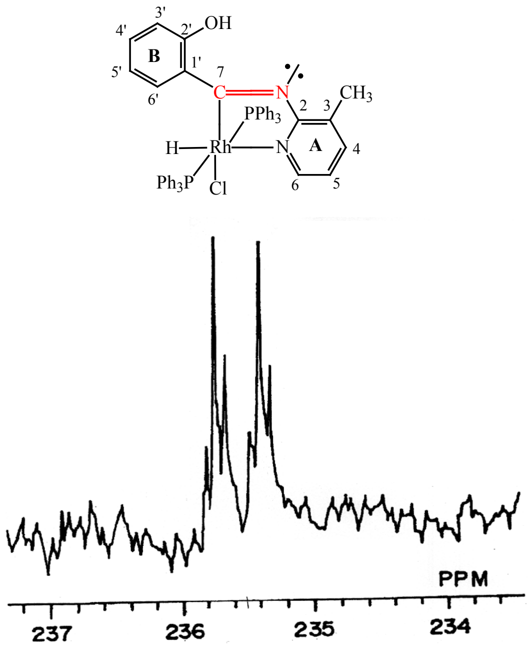


Figure 6: 13C-NMR spectra for complex (17).

with 1,5-hexadiene in toluene at 110°C for 6 h under [RhCl $(PPh_3)_3$] in screw-capped vial, gives only imonoacyl rhodium(III) complex. The chromatographic results show no indication of forming hex-5ˋ-enylketimine. These results indicated that the bond between rhodium and hydrogen is not active enough, very stable and can't go for further reactions.

Conclusion

The new cyclometallated rhodium complexes have been characterized by elemental analysis, UV, IR, ^{1}H, ^{31}P (occasionally) and ^{13}C-NMR-spectroscopy. Interestingly the hydride ligand signal in IR (v 2034.9 cm^{-1} and ^{1}H-NMR (δ -11.29 ppm), complex (22). The result obtained from the spectra was expected for Rh-H group trans position to the N-donor ligand.

However, the ^{31}P-NMR for some cyclometallated complexes shows signal at δ 31.86ppm, complex (22). Furthermore, the ^{2}J (^{31}P-1H) value account for H cis to two magnetically equivalent PPh_3-groups, which in turn are mutually trans, as inferred from ^{31}P(1H) NMR spectrum. This result is supported from ^{1}H and ^{13}C NMR spectra.

Interestingly, the ^{13}C-NMR of the iminoyl carbon (^{13}C=N) signal in Rh(III) (δ 225.16-237.60 ppm). This low-field position for cyclometallated complexes is suggestive of carbene-like properties. The result from the study indicated that the bond between rhodium and hydrogen is not active enough, very stable and can't go for further reactions.

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