

Hydridothiazole Rhodium Complexes as a Result of C-H Bond Activation in Iminothiazoles Chelating Ligands

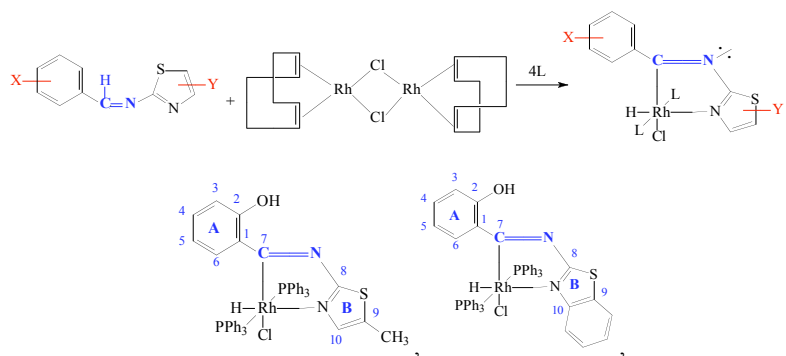
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Abstract: A series of 20 Schiff base ligands derived from 2-aminothiazole and its derivatives and aryl aldehydes with either $[\text{RhCl}(\text{PPh}_3)_3]$ or $[\text{Rh}(\mu\text{-Cl})(\text{COD})_2]$ in the presence of 4 equivalents of PPh_3 lead to an Rh(III) cyclometallated complex and the imine ligand (C-H) bond has been added to the metal (C-M-H). The complexes were investigated by using I.R., ^1H , ^{13}C and ^{31}P NMR Spectroscopic techniques. The signal of the (C-H) ligand was observed as trans to the nitrogen atom in the complex which is a donor ligand.

Graphical Abstract: Total synthesis of hydridothiazole rhodium complexes possessing rhodium hydride signal at δ (-14.60 to -15.04) ppm, trans to N-donor ligand and iminoyl carbon ($^{13}\text{C}=\text{N}$) signal in Rh (III) observed at δ (220.1-237.6) ppm, lower field and suggestive of carbene like properties.



Iminothiazoles chelating ligands + $[\text{Rh}(\mu\text{-Cl})(\text{COD})_2]$

Keywords: Hydrido complexes, ligand substitution, IR, ^1H , ^{13}C , ^{31}P NMR, oxidative-addition, phosphine complexes, rhodium, Schiff-bases.

1. INTRODUCTION

The oxidative addition of C-H bond activated by transition metal has been reported in many recent studies in organometallic chemistry [1-4]. Benzylic imines ($\text{Ph-CH}=\text{NR}$) are the most studied ligands in the cyclometallation of transition metals [5, 6]. It has been reported that intramolecular C-H activation examples of rhodium with N-donor ligands and C-X (X: halogen) activation with imines [2-4, 7-9]. The first report of ortho-metallation of imines at rhodium *via* C-H activation has appeared only recently [2-4, 10]. Interestingly, cyclometallation reaction of imine [11] C-H bonds leads us to study some of the important chemistry related to the imines, derivatives from 2-aminothiazole and its derivatives and aryl aldehydes. 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 [12-16]. Chung-Hang Leung and Dik-Lung Ma group have also actively pursued the development of kinetically inert metal complexes as inhibitors of various bimolecular targets, including DNA, enzymes and protein-protein interactions [13]. Here, we report the synthesis and characterization of many new rhodium (III) complexes of (X - (substituted benzyldene amino) thiazoles.

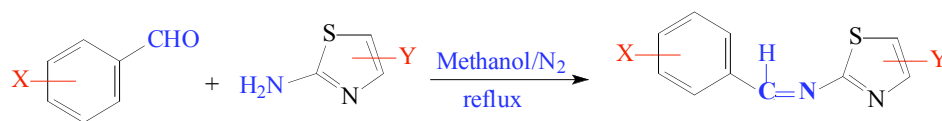
2. MATERIAL AND METHODOLOGY

CHEMICALS: All techniques and operations were performed under nitrogen using Schlenk techniques. Substituted aryl aldehydes, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, Ph_3P , cyclo-1, 5-octadien, and 2- aminothiazoles derivatives were purchased from Winlab, Aldrich and Strem chemicals, and were used as received.

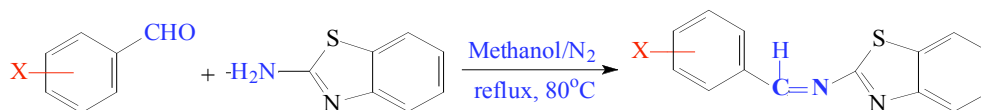
2.1. Schiff Bases Syntheses

The Schiff bases were synthesized by adding equivalent amounts of aryl aldehydes and 2-aminothiazole derivatives

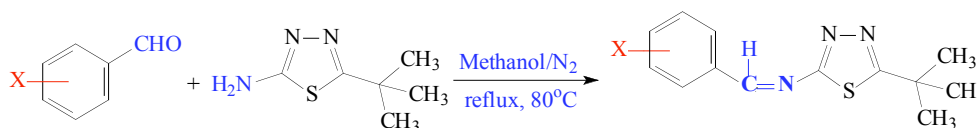
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Eq. (1). Describes schematic diagram for the preparation of Schiff bases (No. 1-15): X, 1 = -H, 2 = 2-OH, 3 = 4-NO₂, 4 = 4-Br, 5 = 3-OH, 6 = 2-NO₂, 7 = 3-Me (compounds from: 1-7, Y = H) 8, Y = 4-CH₃ (X = H), 9, Y = 4-Me (X = 2-OH), 10, Y = 4-Me (X = 4-NO₂), 11, Y = 4-Me, (X = 4-Br), 12, Y = 5-Me, (X = H), 13, Y = 5-Me, (X = 2-OH), 14, Y = 5-Me, (X = 4-NO₂), 15, Y = 5-Me, (X = 4-Br).



Eq. (2). Compound (No.16), X = 2-OH.



Eq. (3). Compound (No.17):, X = H,(18), X = 2-OH,(19), X = 4-NO₂, (20), X = 4-Br.

in 80 ml methanol. The resulting mixture was boiled under reflux and stirred for 9 h at 80°C in an oil bath, and then the solvent was concentrated by using rotary evaporation to give brown viscous liquid. Then n-hexane was added to precipitate the crude product, which was then recrystallized in dichloromethane and with n-hexane to give white precipitate, dried, yield 50-70% scheme (1), (the full characterization of the resulting Schiff base was submitted for publication in Arab Gulf Journal of Scientific Research (AGJSR), 2014.

2.2. Syntheses of the Cyclometallated Schiff Base Complexes

The rhodium (III) complexes were synthesized by reaction of the Schiff base with either {RhCl(Ph₃P)₃} or [Rh(μ-Cl)(COD)]₂. [17, 18]. Here, we report two examples:

- A solution of {Rh Cl(PPh₃)₃} (300 mg, 0.325 mmol) mixed with an equivalent amount of thiazole imines in 20 cm of dry THF was refluxed for 1 h under nitrogen atmosphere, then allowed to cool. Addition of n-hexane precipitated the product, the resulting product gave yellow solid, which was separated and (recrystallized from CH₂Cl₂/hexane).
- A solution of {Rh(μCl)(COD)}₂ (200 mg, 0.28 mmol), thiazole Schiff base (0.56 mmol) and PPh₃ (293 mg, 1.12 mmol) in ca. 20 cm³ of dry THF was refluxed for 1 h, and by addition of n-hexane, the product was precipitated, which was separated by filtration and (recrystallized from CH₂Cl₂/hexane).

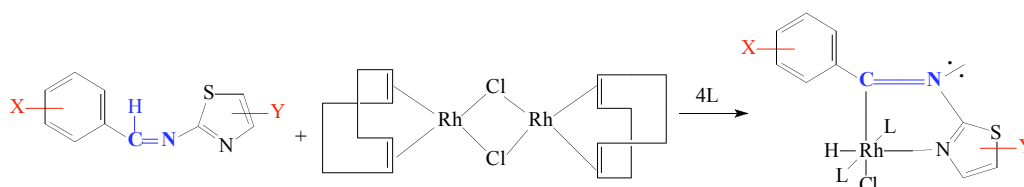
2.3. Spectroscopy

I.R. spectra were measured using Nexus spectrophotometer FT IR. The N.M.R. spectra were recorded at R.T. on a JEOL 400 MHz. The ¹H, ¹³C (1H) and ³¹P [1H] -n. m. r. frequencies observed at 400, 100 and 161.08 MHz respectively (at JEOL). Positive values for ³¹P- [1H] representing deshielding. The cyclometallated complexes were dissolved in CDCl₃.

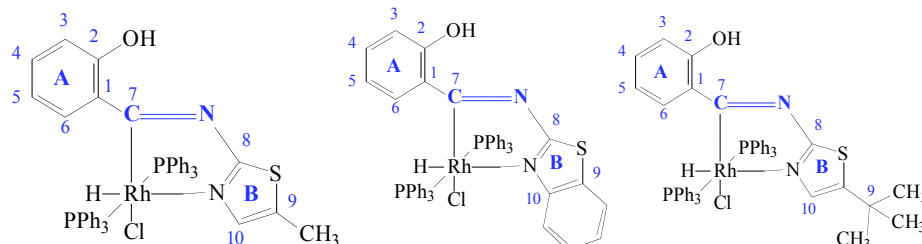
3. RESULTS AND DISCUSSION

Introducing metal into C-H bond have been observed in many compounds like quinoline and Schiff base substrates [19]. A significant amount of work has been done on the heterocyclic aromatic species, 8-substituted quinoline [20-24] and 2- (benzylideneamino) pyridines [25-29]. Coordination of the metal with nitrogen atom in aryl amines results in a favorable geometry for introducing of the metal into neighboring C-H or C-C bond [21, 25, 26, 30]. Rhodium complexes (Table 1) were synthesized either by mixing and refluxing equimolar amount of the Schiff base with {RhCl(Ph₃P)} in THF for 0.5h [31], or by boiling a solution of one equivalent of {Rh(μ-Cl)(COD)}₂, with two equivalents of prepared Schiff base with four equivalents of phosphine in THF for 1h, as showed in Scheme (2). The ¹H NMR spectrum of each of the new rhodium complexes in CDCl₃ shows a hydride resonance between δ -11.49 and δ -13.27 ppm (Table 3). The signals of the starting Schiff bases, C-H observed at δ 8.20-9.44 ppm and in the resulting complex, these signals are absent, providing evidence for insertion of Rh complex 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 [24, 29] ca. δ -12.38 ppm. The hydride signals in the complexes are split by coupling to an equivalent of two ³¹P nuclei and the ¹⁰³Rh nucleus. The spin-spin couplings are frequently ca. 12.0 Hz, the hydride multiplet observed as a pseudo quartet, but higher resolution frequency are usually appear as the expected doublet of triplets. The ³¹P, of rhodium complexes show a ³¹P signal at ca. δ 28.2-37.78 with 1J (¹⁰³Rh-³¹P) 102.00-120.00 Hz as a doublet (Table 3) in keeping with previous report [30]. The majority of the rhodium imines hydride complexes are only moderately soluble in chloroform-d and dichloromethane-d₂ solvents (complexes are soluble in DMSO, but decomposed during NMR processing).

The ¹³C [1H] NMR spectrum, in particular the signal from the metal- carbon bonded atom, is consistent with the presence of the cyclometallated ring [24, 31, 32] the signal



Scheme 1. Describes Schematic preparation and structural of iminothiazoles (1-20) chelating ligands.



Scheme 2. Describes schematic diagram for preparation of "hydridothiazole" rhodium complexes.

Table 1. Describes the rhodium complexes obtained from Schiff bases derived from 2-amino thiazoles and benzaldehydes (complexes No. (21-29), 2-aminobenzothiazole and benzaldehyde (complex 30) and 2-amino-5-t-butyl-1, 3, 4-thiadiazole and benzaldehydes (complex 31).

Complex No.	X	Y	Complex No.	X	Y
21	H	H	27	4-NO ₂	4-Me
22	2-OH	H	28	H	5-Me
23	4-NO ₂	H	29	2-OH	5-Me
24	4-Br	H	30	2-OH	1*
25	2-OH	4-Me	31	2-OH	2*
26	H	4-Me			

Table 2. CHN-Elemental Analyses for Complexes No. (21-31).

No.	X	M.P. (°C)	M.F.	Calculated (%)			Found (%)		
				C	H	N	C	H	N
21.	H	162	RhC ₄₆ H ₃₈ N ₂ SP ₂ Cl	64.9	4.51	3.3	65.30	4.63	3.40
22.	2-OH	190	RhC ₄₆ H ₃₈ N ₂ SOP ₂ Cl	63.70	4.53	3.23	64.70	5.01	3.34
23.	4-NO ₂	185	RhC ₄₆ H ₃₇ N ₃ SO ₂ P ₂ Cl	61.7	4.16	4.7	60.66	4.26	4.34
24	4-Br	192	RhC ₄₆ H ₃₇ N ₂ SP ₂ ClBr	59.40	4.00	3.00	60.40	4.30	3.32
25.	H	202	RhC ₄₇ H ₄₀ N ₂ SP ₂ Cl	65.24	4.65	3.23	64.98	3.93	3.7
26.	2-OH	192	RhC ₄₇ H ₄₀ N ₂ SOP ₂ Cl	64.06	4.89	3.17	63.13	4.44	2.95
27.	4-NO ₂	214	RhC ₄₇ H ₄₀ N ₃ SO ₂ P ₂ Cl	60.63	4.42	4.61	60.33	4.38	4.53
28.	H	198	RhC ₄₇ H ₄₁ N ₂ SP ₂ Cl	65.24	4.65	3.23	64.98	3.93	3.7
29.	2-OH	200	RhC ₄₇ H ₄₂ N ₂ SOP ₂ Cl	64.06	4.89	3.17	64.2	4.13	3.52
30.	2-OH	70	RhC ₅₀ H ₄₀ N ₂ SOP ₂ Cl	66.63	4.47	3.11	65.98	4.35	3.93
31.	2-OH	160	RhC ₄₉ H ₄₆ N ₃ SOP ₂ Cl	64.47	5.09	4.62	65.01	4.89	4.35

Table 3. ^1H , and ^{31}P -N.M.R. chemical shifts and $^2\text{J} (^{31}\text{P}-^1\text{H})$, $^1\text{J} (^{103}\text{Rh}-^1\text{H})$ and $^1\text{J} (^{103}\text{Rh}-^{31}\text{P})$ coupling constants of complexes No. (21-31). (In CDCl_3).

Comp. No.	X	Y	$\delta^1\text{H}$ Hydride (p.p.m.)	$\delta^{31}\text{P}\{^1\text{H}\}$ (p.p.m.)	$^2\text{J} (^{31}\text{P}-^1\text{H})$ (Hz)	$^1\text{J} (^{103}\text{Rh}-^1\text{H})$ (Hz)	$^1\text{J} (^{103}\text{Rh}-^{31}\text{P})$ (Hz)
21.	H	H	-12.09	28.7	12.0	12.4	102
22.	2-OH	H	-12.30	31.4	12.0	12.4	107
23.	4-NO ₂	H	-12.05	29.0	12.0	12.7	107
24.	4-Br	H	-12.16	28.2	12.0	12.5	103
25.	3-OH	4-Me	-12.36	32.35	12.0	12.50	111
26.	H	4-Me	-13.27	29.51	12.0	12.45	108
27.	4-NO ₂	4-Me	-13.27	29.60	12.0	12.54	111
28.	H	5-Me	-12.15	32.30	11.0	12.50	111
29.	2-OH	5-Me	-12.36	32.33	11.0	12.45	111
30.	2-OH	-	-13.08	29.20	11.0	13.3	120
31.	2-OH	-	-11.49 -12.36	37.87 29.54	11.0 11.0	12.50 12.80	111 118

Table 4. ^{13}C -NMR chemical shifts for C (7) (iminoyl carbon- $^{13}\text{C}=\text{N}$), and coupling constants $^1\text{J} (^{103}\text{Rh}-^{31}\text{P})$ Hz and $^2\text{J} (^{103}\text{Rh}-^{31}\text{P})$ Hz.

Complex No.	X	C(7) (ppm)	$^1\text{J} (^{103}\text{Rh}-^{31}\text{P})$ (Hz)	$^2\text{J} (^{103}\text{Rh}-^{31}\text{P})$ (Hz)
21.	H	220.1	33	8
22.	2-OH	222.8	32	8
23.	4-NO ₂	224.1	33	8
24.	4-Br	222.0	32	9

from the metal-bonded carbon, C (7) (iminoyl carbon- $^{13}\text{C}=\text{N}$) appears as a doublet of triplets owing to coupling to two equivalent ^{31}P nuclei and the ^{103}Rh nucleus, whereas the corresponding signal from the uncomplexed Schiff base was found at δ 159.25-164.97 ppm [24]. For C (7), δ - has been observed at low-field position in which a chelating atom is incorporated in a five member-ring [33], and this was expected for a cyclometallated sp^2 carbon [11, 34] (similar to carbene-carbon. The remaining ^1H and ^{13}C NMR data are as expected. Table 4, demonstrate the ^{13}C -NMR chemical shifts for C (7) (iminoyl carbon- $^{13}\text{C}=\text{N}$), and coupling constants $^1\text{J} (^{103}\text{Rh}-^{31}\text{P})$ Hz and $^2\text{J} (^{103}\text{Rh}-^{31}\text{P})$ Hz. Complex No. X, C (7) (ppm) $^1\text{J} (^{103}\text{Rh}-^{31}\text{P})$ (Hz) $^2\text{J} (^{103}\text{Rh}-^{31}\text{P})$ (Hz), respectively. No. 21, X = H; 220.1; 33; 8. No 22; X = 2-OH; 222.8; 32; 8. No.23; X = 4-NO₂; 224.1; 33. 8. No. 24; X = 4-Br; 222.0 ; 32.0; 9. The positions of the Rh-H signals in both IR (ν Rh-H) 2073.48 cm^{-1} for compound (24) and ^1H NMR (δ -11.49 to -13.27 ppm) spectra, are as expected for a Rh-H bond located trans to the nitrogen-donor ligand. In addition, the $^2\text{J} (^{31}\text{P}-^1\text{H})$ value is consistent with a hydride located cis to two magnetically equivalent of PPh_3 groups [35-37], which in

turn are mutually trans, as confirmed from the ^{31}P (^1H) NMR spectrum. Interestingly, the hydride ^1H NMR spectrum of compound (31) presented in two types of the hydride spectrum which appear at δ -11.49 ppm and -12.36 ppm. Also, two ^{31}P -spectrum appears at δ 37.87 ppm and δ 29.54 ppm with $^2\text{J} (^{31}\text{P}-^1\text{H})$, 11.0 and 11.0 Hz and $^1\text{J} (^{103}\text{Rh}-^1\text{H})$ 12.50 Hz and 12.80 Hz with $^1\text{J} (^{103}\text{Rh}-^{31}\text{P})$, of 111 Hz and 118 Hz respectively. This result may be due to the presence of *t*-butyl group at C-5 of the thiazole ring, which leads to different geometric structure. It was also observed that the signal for C (7) (iminoyl carbon- $^{13}\text{C}=\text{N}$) is at low magnetic field, at δ 224.1 ppm, this may be due to the substitution of 4-NO₂ (at para-position in aryl ring), as electron withdrawing group, which leads to decrease in the electronic density on C-7 led δ -moved to low magnetic field, compared with other groups on aryl ring of the same complexes.

CONCLUSION

The new cyclometallated complexes have been characterized by elemental analysis, IR, ^1H , ^{13}C -NMR and ^{31}P (only the more soluble complexes were recorded in CDCl_3) spec-

trospectroscopy. Interestingly, the hydride ligand signals in both IR (2040 cm^{-1}) and $^1\text{H-NMR}$, δ ((-14.60) – (-15.04)) ppm. The result obtained from the spectra was expected for Rh-hydride atom trans position to the N-donor ligand. However, the $^{31}\text{P-NMR}$ for some cyclometallated complexes shows signal at δ (30.20-34.67) ppm. The 2J ($^{31}\text{P-H}$) value consistent for H cis is to two magnetically equivalent PPh_3 -groups, which indicate mutually trans, as observed from the ^{31}P (^1H) NMR spectrum. This result supported from ^1H and $^{13}\text{C-NMR}$ spectra. Interestingly, the $^{13}\text{C-NMR}$ of the iminoyl carbon ($7\text{C}=\text{N}$) signal in Rh (III) observed at δ (220.1-237.6) ppm. This low-field position for cyclometallated complexes is suggestive of carbene-like properties.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

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