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Novel Unreactive Hydrido-Iminoyl Complexes of Rhodium(III) with Some Schiff Bases Derived from Quinoline-8-Carbaldehyde and Alkylamines

Hassan B. Amin

Department of Chemistry, College of Science
King Saud University, P.O.Box 2455, Riyadh - 11451, Saudi Arabia

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Abstract. A series of rhodium(III) cyclometallated complexes of the type $[RhHCl(NC_9H_6C{=}NR)(PPh_3)_2]$ have been synthesised and characterized. Schiff bases derived from an alkylamine and quinoline-8-carbaldehyde were allowed to react with $[RhCl(PPh_3)_3]$ to give Rh^{III} cyclometallated complexes, in which the imine C-H added oxidatively to the metal. These complexes reacted with reagents such as CN^-, CO, $P(OCH_3)_3$, to give substitution product in which the Cl has been replaced. The complexes were characterized using ir and n.m.r. spectroscopies and confirmed by elemental microanalysis.

Introduction

Although the cyclometallation of aromatic and, to a lesser extent aliphatic C-H groups is widely recognized[1,2], there is relatively little known concerning with the cyclometallation of aldehydes[3] and imine functions[4-6]. We have shown that Schiff bases of 2-(benzylidenamino) pyridines[6], and 2-substituted benzylidenaminothiazoles[5] can be made to cyclometallate at the imine carbon by using Rh^I complex. A number of studies have exploited ligands such as quinoline-8-carbaldehyde[3,7] and 2-(benzylidenamino) pyridines[8]. Complexation of the metal with aromatic nitrogen gives a favorable geometry for the insertion of the metal into the neighbouring C-R group [4,7,9].

The synthesis and characterization of a variety of new rhodium(III) complexes of N-(quinolidino)alkylamine (Scheme 1-a), in which the imine C-H has undergone oxidative addition to the metal are reported here.

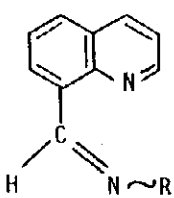
Experimental

Quinoline-8-carbaldehyde, $RhCl_3.XH_2O$, triphenylphosphine, tetrahydrofuran (THF), cyclo-1,5-octadiene(COD), and amines were obtained from Winlab, Aldrich Chemicals and Strem Chemicals, respectively and were used without further purification.

The Schiff bases were prepared by mixing equivalent amounts of quinoline-8-carbaldehyde and primary amines in dry benzene (70 cm^3). This mixture was heated under reflux with stirring for 5 h in an oil bath and the water produced during the reaction was collected by Dean-Stark trap. The remaining solution was concentrated by rotary evaporation to give a brown viscous liquid. This was treated with hexane to precipitate the crude product, which was then distilled in vacuo to give the pure imine, Table 1.

The ^1H- and ^{13}C- NMR data is presented in Table 2. $[RhCl(COD)]_2$ and $[RhCl(PPh_3)_3]$ were prepared by literature procedures[10,11].

Table 1. Physical and microanalytical properties of Schiff bases



R	B.P.C°/ mm Hg	Yield %	Molecular formula	Calculated (%) C	H	N	Found (%) C	H	N
^{i}Pr	99/0.3	88	$C_{13}N_{14}N_2$	78.5	7.12	14.13	78.63	7.10	14.20
^{n}Bu	130/0.4	92	$C_{14}H_{16}N_2$	79.20	7.60	13.20	79.10	7.48	13.21
^{i}Bu	119/0.7	94	$C_{14}H_{16}N_2$	79.20	7.60	13.20	79.25	7.55	13.15
^{s}Bu	72/0.2	79	$C_{14}H_{16}N_2$	79.20	7.60	13.20	79.19	7.62	13.18
^{t}Bu	132/0.6	85	$C_{14}H_{16}N_2$	79.20	7.60	13.20	79.24	7.57	13.31
Benzyl	74*	91	$C_{17}H_{14}N_2$	82.89	5.73	11.38	82.84	5.55	11.43
(+) Methylbenzyl	152/0.1	90	$C_{18}H_{16}N_2$	83.04	6.20	10.76	82.94	6.14	10.65
(-) Methylbenzyl	153/0.1	86	$C_{18}H_{16}N_2$	83.04	6.20	10.76	83.23	6.31	10.72

*m.p.: recrzyst. from ethanol

Table 2. ^{1}H and ^{13}C n.m.r. chemical shifts (ppm from TMS) for the Schiff bases derived from the reaction of quinoline-8-carbaldehyde and amines

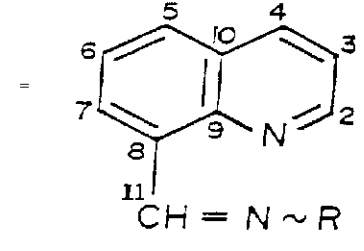
Compound		C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C	CH	CH_2	CH_2	CH_2	CH_3	CHO (CN=N)
	^{1}H	9.00	←			→	7.40(c)*					←			R		→
11.4(s)																	
1) 8-CHO																	
	^{13}C	151.3	121.8	136.3	134.3	126.2	129.2	131.6	147.5	128.3							192.6
	^{1}H	8.9	←			→	7.3(c)					3.8				1.3(d)	9.7(s)
2) imine R= ^{i}Pr	^{13}C	149.9	121.1	136.3	130.0	126.5	127.6	133.4	146.6	128.3		61.9				24.3	156.1
	^{1}H	9.0	←			→	7.4(C)						3.8(t)	1.7(m)	1.4(m)	1.0(t)	9.6(s)
3) ^{n}Bu	^{13}C	149.7	121.1	136.2	130.0	126.4	127.3	133.2	146.5	128.2			61.8	33.2	20.6	14.0	158.4
	^{1}H	9.0	←			→	7.3(C)					2.1(m)		3.6(d)		1.0(d)	9.6(s)
4) ^{i}Bu	^{13}C	150.0	121.2	136.3	130.1	126.6	127.5	133.3	146.7	128.3		29.8		70.1		20.9	158.6
	^{1}H	9.0	←			→	7.3(C)					3.5(m)	1.7(m)			1.3(d)	9.6(s)
5) ^{t}Bu																11.2	
	^{13}C	150.0	121.2	136.3	130.0	126.6	127.7	133.4	146.7	128.2		68.5		30.9		11.2	156.6

Continued .....

Table 2. *(Continued)*

Compound		C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C	CH	CH_2	CH_2	CH_2	CH_3	CHO (CH=N)
6) ^{t}Bu	^{1}H	8.9	⟷				7.3(C)									1.4(s)	9.7(s)
	^{13}C	149.8	121.1	136.2	129.7	126.5	127.1	134.2	146.7	128.3	58.0					30.9	153.3
7) Benzyl	^{1}H	8.9	⟷				7.3 (C)							5.0(s)			9.8(s)
	^{13}C	150.0	121.2	136.2	130.4	126.3	128.0	132.8	146.5	128.4	Ph(C′-1, 139.6; C′-2, 128.4; C′-3, 127.3; C′-4, 126.8			65.6			159.6
8) (-)α(Me)-benzyl	^{1}H	8.9	⟷				7.3(C)					4.8(q)				1.7(d)	9.8(s)
	^{13}C	150.0	121.2	136.3	130.2	126.5	127.7	133.2	146.6	128.4		Ph(C′-1, 145.5; C′-2, 127.7; C′-3, 126.7; 70.3 C′-4, 126.5)				25.0	157.1
9) (+)α(Me)-benzyl	^{1}H	8.9	⟷				7.3(C)					4.8(q) Ph(C′-1, 145.5; C′-2, 127.7; C′-3, 126.7; C′-4, 126.5)					9.8(s)
	^{13}C	150.0	121.2	136.3	130.2	126.5	127.7	133.2	146.6	128.4		70.3					157.1

*(c) = Complex



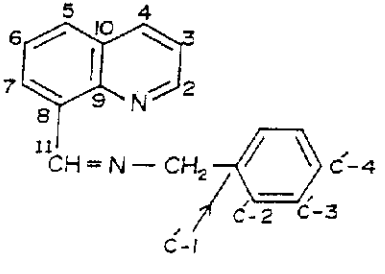
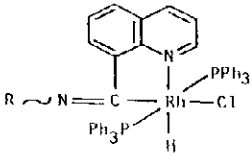


Table 3. Physical and microanalytical properties of cyclometallated complexes



R	M.P°C	Yield	Molecular	Calculated (%)			Found (%)		
		%	formula	C	H	N	C	H	N
^{i}Pr	192	80	$C_{49}H_{44}N_2ClP_2Rh$	68.34	5.15	3.25	68.25	5.24	3.30
^{n}Bu	185	87	$C_{50}H_{46}N_2ClP_2Rh$	68.61	5.30	3.20	68.64	5.32	3.17
^{t}Bu	135	78	$C_{50}H_{46}N_2ClP_2Rh$	68.61	5.30	3.20	68.56	5.23	3.24
^{s}Bu	165	85	$C_{50}H_{46}N_2ClP_2Rh$	68.61	5.30	3.20	68.61	5.34	3.21
^{i}Bu	170	90	$C_{50}H_{46}N_2ClP_2Rh$	68.61	5.30	3.20	68.58	5.28	3.27
Benzyl	145	85	$C_{53}H_{44}N_2ClP_2Rh$	70.00	4.88	3.08	70.03	4.75	3.12
(-) Methylbenzyl	215	82	$C_{54}H_{46}N_2ClP_2Rh$	70.25	5.02	3.03	70.27	5.10	3.10
(-) Methylbenzyl	215	87	$C_{54}H_{46}N_2ClP_2Rh$	70.25	5.02	3.03	70.31	5.23	3.11

Preparation of cyclometallated schiff's base complexes

The rhodium(III) complexes were prepared by reaction of the Schiff base with either $RhCl(PPh_3)_3$ or with $[\{RhCl(COD)\}]_2$. Two typical examples are described below.

1) A solution containing $[RhCl(PPh_3)_3]$ (300 mg, 0.325 mmol) and an equivalent amount of Schiff base in *ca.* 20cm^3 of dry THF was heated under reflux for 1 h under a nitrogen atmosphere. After cooling, addition of hexane led to precipitation of the product as a yellow powder, which was filtered off (the product could be recrystallized from CH_2Cl_2/ hexane), Table 3.

2) A solution of $[\{Rh(\mu\text{-}Cl)(COD)\}]_2$ (200 mg, 0.28 mmol), Schiff base (0.56 mmol) and PPh_3 (293 mg, 1.12 mmol) in *ca.* 20cm^3 of dry THF was heated under reflux for 1h. Addition of hexane induced precipitation of the product, which was filtered off (the product could be recrystallized from CH_2Cl_2/hexane), Table 3.

Spectroscopy

U.V.-Vis spectra were recorded on a Pu-8800 Pye Unicam Phillips spectrometer using spectroscopic grade solvents (MeOH, EtOH and $CHCl_3$). Ir spectra were measured using a Perkin-Elmer 783 spectrophotometer, using KBr pellets for solid compounds and neat liquid compounds between KBr plates. N.m.r. spectra were measured at 25°C on a Jeol FX-400 FT spectrometer using deuterium locking. $^{13}C\{^1H\}$ n.m.r. observation frequency, 100 MHz; ^1H- n.m.r. observation frequency, 400 MHz; $^{31}P\{^1H\}$ spectra were recorded at

161.83 MHz. Chemical shift data for ^{31}P spectra are given relative to 85% H_3PO_4 (external), more positive values representing deshielding. The cyclometallated compounds were dissolved in $CDCl_3$.

Results and Discussion

Complexes shown in [Scheme 1-b] were prepared either by heating under reflux equimolar amounts of the Schiff base with $[RhCl(PPh_3)_3]$ in THF for 0.5h, or by refluxing a solution of one equivalent of $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$, two equivalents of Schiff base and four equivalents of phosphine in THF.

The ^1H n.m.r. spectra of the rhodium complexes show a hydride resonance between -12.0 and -12.4 (Table 4). The imine C-H signals for the free Schiff bases appear at δ (9.66 - 9.77) (Table 2); after complexation these signals are absent. Complex(B) shows splitting of the hydride resonance by two equivalent ^{31}P spins and the ^{103}Rh. As both of these spin-spin couplings are frequently in the range of 10-16Hz, the hydride multiplet often appears as a pseudo-quartet[3]; resolution studies usually reveal the expected doublet of triplets (Fig. 1).

The rhodium(III) hydride complexes(B) show a $^{31}P\{^1H\}$ signal in the range δ 28-32 p.p.m. with $^1J(^{103}Rh, ^{31}P)$ 102-106 Hz, in keeping with the literature [12, 13]. Further support for cyclometallation comes from the ^{13}C n.m.r. data. The complexes(B) are only moderately soluble, and only a few ^{13}C spectra were obtained; these data are shown in

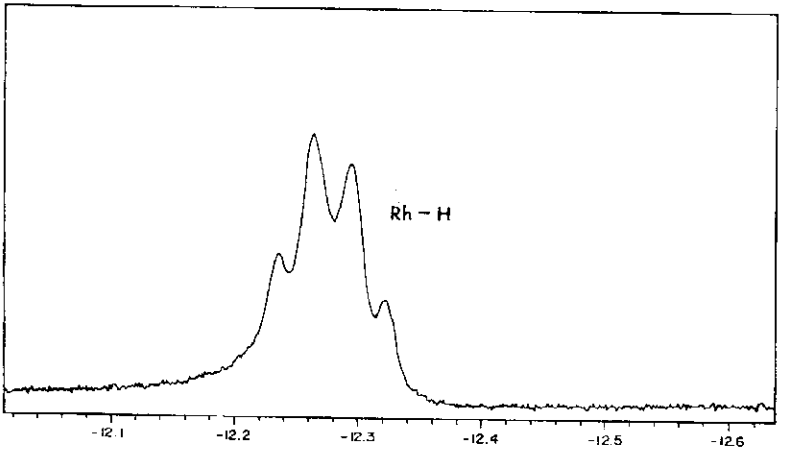


Fig. 1. 400 MHz ^1H NMR spectrum of complex (4) (0.1 M in $CDCl_3$ at 25°C).

Table 5. The signals for iminoyl carbon, $^{13}C{=}N$, (Scheme 1-b) are all at 220-224 p.p.m. whereas the uncomplexed imine C=N signal is found at δ 156-160 p.p.m. [14] (Table 2). This low-field position for C=N, has been observed in other cases where a chelating atom is incorporated in a five-membered ring[15], and is not unusual for cyclometallated sp^2 carbon[16,17]. The rest of the ^1H and ^{13}C n.m.r. data are also as expected.

Interestingly, the hydride ligand signals, in both the ir (ν (Rh-H) 2040cm^{-1}) and ^1H n.m.r. (δ-12.0 to -12.4) spectra, were as expected for a Rh-H group trans to an N-donor ligand[18,19]. Furthermore the $^2J(^{31}P\text{-}^1H)$ value is consistent with a hydride located cis to two magnetically equivalent PPh_3 [20] groups, which in turn are mutually trans, as inferred from the $^{31}P\{^1H\}$ n.m.r. spectrum.

The complexes(B) [Schemes 1(b), and 2], are readily converted to a new series of complexes(C), in which the Cl ligand has been replaced by ligand = CN^-, $P(OCH_3)_3$ or CO. In the last two cases the complexes were isolated as $[PF_6]$ salts. These complexes are novel in that they represent rare examples of stable hydride complexes, with two cis carbon-type ligands, which neither reductively eliminate nor insert the carbon ligand(s) into the metal-hydride bond (further work is under way). The failure of hydride to attack CO or CN^- is not unexpected. This may be due to one or more of the following facts: a) complex (B) is octahedral d^6 species, whose reactions may be relatively slow; b) the molecule has a

Table 4. ^1H and ^{31}P n.m.r. chemical shifts (ppm) and coupling constants(Hz) of the cyclometallated complexes

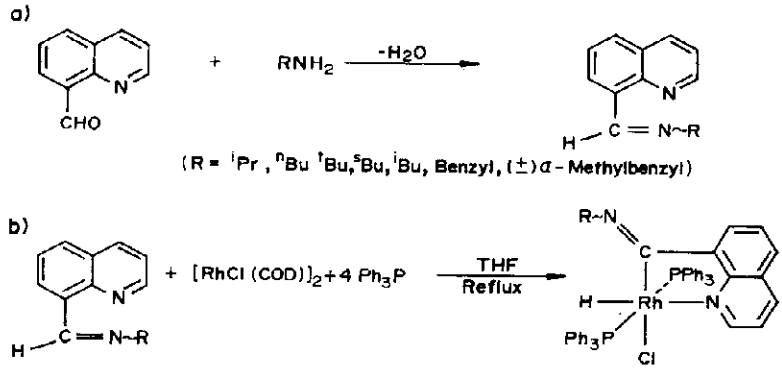
Complex	^1H Hydride	$^{31}P\{^1H\}$	$^2J(^{31}P\ ^1H)$	$^1J(^{103}Rh\text{-}^1H)$	$^1J(^{103}Rh\text{-}^{31}P)$
2*	-12.20	28.50	12.0	12.4	103
3	-12.28	30.70	12.0	12.4	103
4	-12.28	32.06	12.0	12.5	107
5	-12.28	32.00	12.0	12.6	107
6	-12.30	32.20	12.0	12.6	107
7	-12.40	32.00	12.0	12.6	105
8	-12.23	31.80	12.0	12.8	105

* Number 2 to 8, represent the cyclometallated complexes derived from Schiff's bases which are shown in Table 1.

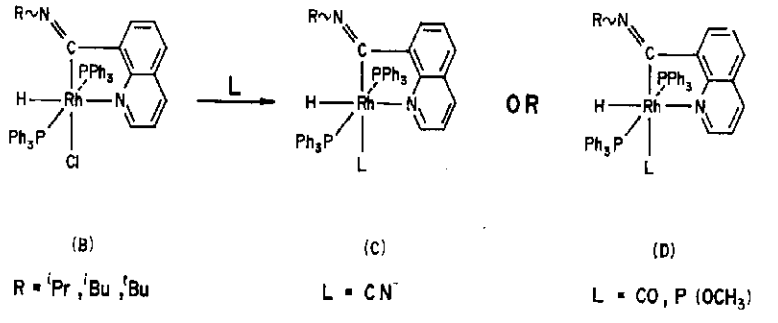
Table 5. Selected $^{13}C\{^1H\}$data for the imine carbon C_{11} in the cyclometallated complexes Chemical shifts (ppm) and coupling constants (Hz)

Complex	δC_{11}	$^1J(^{103}Rh\text{-}^{13}C)$	$^2J(^{31}P\text{-}^{13}C)$
2*	230.4	33	8
4	232.0	33	8
6	228.0	34	8
7	228.6	33	9

*See table 2.



Scheme 1



Scheme 2

carbon ligand which is part of chelate ring, so may not undergo insertion reactions as readily as a monodentate carbon ligand; and c) in some cases carbon ligands attached to electron withdrawing groups insert relatively slowly. However, there is precedence for isonitrile insertion into a Rh^{III}-H bond [20].

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تحضير مركبات جديدة وغير فعالة للروديوم (III) مع بعض قواعد شيف من - الكيلات ايمين المشتقة من كينولين - ٨ - كاربالدهيد

حسان بن بكر أمين

جامعة الملك سعود - كلية العلوم - قسم الكيمياء ص.ب. ٢٤٥٥
الرياض ١١٤٥١ المملكة العربية السعودية
(استلم في ٥/٦/١٤١٨هـ؛ وقبل للنشر في ٧/١/١٤١٩هـ)

ملخص البحث. تم تحضير سلسلة من معقدات الروديوم المحلقنة من النوع :

$$[RhHCl\,(NC_9H_6C{=}NR)\,(PPh_3)_2]$$

وذلك بتفاعل قواعد شيف المشتقة من الكيلات ايمين وكينولين - ٨ - كاربالدهيد، وقد وجد أن هيدروجين مجموعة الأيمين ارتبط على شكل هيدريد مع الروديوم الذي ارتبط مع كربون مجموعة الأيمين لحدوث عمليتي الأكسدة والحلقنه. كما أن المركبات المعقدة تفاعلت مع $P(OCH_3)$, CO, CN^- وتم احلالها بدلاً من Cl الموجود في المعقد. وتم التعرف على جميع المعقدات السابقة بواسطة الأشعة تحت الحمراء والرنين النووي المغناطيسي ودعمت عن طريق التحليل العنصري لها.